THE CHEMISTRY OF ETHYNYL, OLEFIN AND CARBENE COMPLEXES OF GOLD AND PLATINUM.

by

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ABSTRACT

Gold Ethynyl complexes, $[Au(C{\equiv}CR)L]$, ($L = PPh_3$, R = H, Me, Et, Ph or CF_3; $L = P(C_6H_4Me\text{-}\underline{p})_3$, R = Ph) can be readily produced from phosphinegold chlorides and $RC{\equiv}CH$ in ethanolic sodium ethoxide. When R = H a second reaction will produce the digold species $LAuC{\equiv}CAuL$ ($L = PPh_3, P(C_6H_4Me\text{-}\underline{p})_3$ or $P(C_6H_4OMe\text{-}\underline{p})_3$.) In a similar manner the cylopentadienyl complex $[Au(C_5H_5)PPh_3]$ can be conveniently prepared from $AuClPPh_3$ and C_5H_6 in ethanolic sodium ethoxide. In solution there is rapid exchange of free phosphine with the coordinated phosphine of AuClL and $[Au(C{\equiv}CPh)L]$. The phenylethynyl group of $[Au(C{\equiv}CPh)(PPh_3)]$ will exchange quantitatively with chloride of $HgCl_2$ producing $AuClPPh_3$ and $Hg(C{\equiv}CPh)_2$. When $[Au(C{\equiv}CPh)L]$ ($L = PPh_3, P(C_6H_4Me\text{-}\underline{p})_3$) is allowed to react with <u>cis</u>-$[PtCl_2(CO)(PMePh_2)]$ (2:1 mole ratio) the product is <u>cis</u>-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$ and $AuClPPh_3$. If the same reaction is performed with a 1:1 mole ratio the phenylethynyl group transfers quantitatively to produce $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$, isomer II (Cl <u>trans</u> to L). When followed by low temperature ^{31}P nmr spectroscopy the first step of the reaction is not stereospecific with an initial mixture of $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ (isomers I & II) which then reacts further with <u>cis</u>-$[PtCl_2(CO)(PMePh_2)]$ to give the final product, isomer II. Similar transfer reactions were used to produce cis-$[Pt(C{\equiv}CCF_3)_2(CO)(PMePh_2)]$ from $[Au(C{\equiv}CCF_3)PPh_3]$ and $[PtCl(C_5H_5)(CO)(PMePh_2)]$ (isomer I, Cl <u>trans</u> to CO) from $[Au(C_5H_5)(PPh_3)]$.

Complexes of the form <u>cis</u>-$[Pt(C{\equiv}CPh)_2L_2]$ ($L = PPh_3$, $PMePh_2$) were prepared from the reaction of $PhC{\equiv}CH$ and <u>cis</u>-$[PtCl_2L_2]$ with EtONa, from CO displacement by L in <u>cis</u>-$[Pt(C{\equiv}CPh)_2(CO)L]$ and from phosphine displacement of 1,5 cyclooctadiene (cod) in $[Pt(C{\equiv}CPh)_2(cod)]$. This latter compound was itself prepared from $[PtCl_2(cod)]$, $HC{\equiv}CPh$ and EtONa.

However, reaction of cis-$[PtCl_2L_2]$ with $Hg(C{\equiv}CPh)_2$ or $HC{\equiv}CPh$ in the presence of CuI produced the thermodynamically favoured trans form of the bis(ethynyl) product. With $[Au(C{\equiv}CPh)PPh_3]$ the result was usually the trans isomer although on one occasion the cis isomer was observed. The routes that produced cis isomers were not generally applicable as different ethynyls (C_2H_2, $HC{\equiv}CMe$) or phosphines (PMe_2Ph) led either to a lack of reaction or trans products. The cis complexes are stable to heat and nucleophiles ($PMePh_2$, I^-). Traces of $HgCl_2$, $HgBr_2$, HgI_2 $HgCl(C{\equiv}CPh)$, HgClPh, CuI, $CuClPPh_3$ or $SnCl_2$ readily convert the cis isomer to the trans form. The mechanism of the reaction (for HgX_2) involved the reversible exchange of ethynyl and chloride groups between metal centres and the very rapid isomerisation of cis-$[Pt(C{\equiv}CPh)XL_2]$.

$[Pt_2Cl_4(PMe_2Ph)_2]$, phenylacetylene and amines (amH = NH_2Ph, $NH_2C_6H_4$-NO_2-p, $NH_2C_6H_4OMe$-m, $NHPh_2$) reacted to produce initially trans-$[(PtCl_2$-$(amH)(PMe_2Ph)]$. Prolonged reaction time formed the neutral amino(organo) carbene platinum complexes cis-$[PtCl_2\{C(am)CH_2Ph\}(PMe_2Ph)]$. Similarly $[Pt_2Cl_4(PBu_3)_2]$ and $[Pt_2Br_2(PMe_2Ph)_2]$ reacted with $HC{\equiv}CPh$ and NH_2Ph to produce cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ and cis-$[PtBr_2\{C(NHPh)CH_2Ph\}PMe_2Ph)]$ respectively. Formation of trans-$[PtCl_2(NHEt_2)(PMe_2Ph)]$ and trans-$[PtCl_2(NH_2Bu^t)(Me_2Ph)]$ was accompanied by disproportionation to cis-$[PtCl_2(PMe_2Ph)]$ and neither complex could be converted to a carbene compound.

The aminocarbene complexes were found to be less reactive than the analogous neutral alkoxy(organo)carbene complexes. No exchange of benzyl protons with CD_3OD or D_2O was observed. The complexes reacted reversibly with Cl^- but no reaction product was isolated. PMe_2Ph and $AgClO_4$ reacted with the aminocarbene to produce trans-$[PtCl\{C(NHPh)CH_2Ph\}(PMe_2Ph)_2]$ ClO_4. The neutral aminocarbene complexes reacted with bases (Et_3N,-EtONa or Bu_4NOH) to form a large number of decomposition products,

although they did not react with "proton sponge"- 1,8-bis(dimethylamino)-napthalene.

The ligands PhN=CHPh, MeN=CHPh, and PhN=CH(C_6H_4Me-o) were prepared from the condensation of the primary amine and the appropriate aldehyde. These imines reacted with [$Pt_2Cl_4(PMe_2Ph)$] to form the Pt-N σ-bonded compounds trans-[$PtCl_2$(im)(PMe_2Ph)]. Trans-[($PtCl_2(NHCPh_2)$-(PMe_2Ph) was similarly prepared, from commercially supplied NH=CPh_2. On standing in $CDCl_3$ solution the imine ligand slowly hydrolysed forming an equilibrium between the platinum amine complex and the imine complex. Aniline and triethylamine displaced PhN=CHPh from trans-[$PtCl_2$ - (NPh=CHPh)(PMe_2Ph)]. The imine complex did not react with EtONa or proton sponge.

The isomerisation reactions of trans-[PtX_2(ol)L] (X = Cl,Br; ol = $C_2H_4C_3H_6$ or C_7H_{14}; L = PBu_3\PMe$_2$Ph) were studied by following the reactions with ^{31}P nmr spectroscopy under a variety of conditions. The trans isomers readily lose olefin and equilibrate with [$Pt_2X_4L_2$]. The position of the equilibria is light sensitive and olefin dependent. The trans isomers steadily isomerise to the cis form. In the presence of excess olefin the rate is reduced for X=Cl and increases slightly for X = Br. In both isomers free olefin exchanges rapidly with co-ordinated olefin. Various pathways are possible for the isomerisation reaction and it was concluded that apart from photochemical processes more than one isomerisation pathway is followed, with a dissociative pathway dominating for the chloride complexes, but an associative pathway preferred for the bromide complexes. Analogous studies were performed on the isomerisation of [PtX_2(dmso)(PBu_3)] (dmso = dimethylsulphoxide) and similar results were obtained which can be related to the similar properties of dmso and olefins bound to Pt(II).

CHAPTER 1.

INTRODUCTION.

The History of Organometallic Chemistry.

Most chemists would think of organometallics as being a modern development in chemistry, dating from around the early 1950's. This is an understandable opinion as it is from that time that the field of organometallics has really expanded, allied with an understanding of the bonding between organic groups and metals and the introduction of new spectroscopic methods, most notable perhaps, being nuclear magnetic resonance (n.m.r.) spectroscopy. However, historically organometallic chemistry began in the early nineteenth century, and up until the 1950's several unrelated developments had taken place.

The first organometallic compound prepared by Zeise in 1827[1] was the platinum olefin complex $K[PtCl_3(C_2H_4)]$, although it was not until 125 years later that the π-bonding nature of the olefin was understood[2]. Frankland[3] in 1850 prepared the first metal alkyl species [ZnI(Et)] whilst trying to generate ethyl radicals in the presence of zinc metal and this complex represents the first organometallic complex to be recognised as such. He subsequently managed to prepare diethyl zinc which was used by Buckton[4] to prepare diethylmercury, tetraethyllead and tetraethyltin from the appropriate metal halides.

Other main group metalalkyls quickly followed, the most notable being those of Grignard[5], who prepared magnesium alkyls [MgBr(R)], the now famous Grignard Reagents, along with the discoveries of Schlenk[6] and Ziegler[7] of the alkali metal alkyls. These very active complexes soon found very many uses as alkylating agents both in organic and organometallic synthesis.

By using these reagents the first transition metal alkyls were prepared. Pope and Peachey[8] used [MgIMe] and [$PtCl_4$] to prepare [$PtI(Me)_3$] and some of its derivatives, whilst [MgBrEt] was found to react with gold(III) halides[9] to produce dimeric gold alkyl, [$AuEt_2(\mu\text{-}Cl)_2]_4$, [$AuEt_2(\mu\text{-}Br)_2]_2$, and [$AuEt_2(\mu\text{-}Br)_2AuBr_2$].

Probably the most significant discovery in organometallic chemistry, and the one which opened up the subject to extensive investigation was the discovery of ferocene in the early 1950's[10,11] and the subsequent elucidation of its "sandwich" structure[12].

In the general growth of research of organometallics, platinum and palladium have received much coverage. This is in part due to interest in the square planar geometry of the divalent complexes of these metals, suitable for studying reaction rates and mechanisms, as well as the high catalytic activity of these metals. Alkylplatinum complexes were reported by Chatt in 1957[13] and in the following two years, extensive series of alkyl and aryl complexes of palladium[14] and platinum[15] were prepared.

That so much effort has been put into understanding organometallic chemistry is not surprising given that not only are the compounds worthy of research for their own sake, but also they have been shown to take part in many chemically useful reactions. These include commercially important catalytic processes where they may be used either as homogeneous catalysts or occur as intermediates in heterogeneous catalysis. As examples of the latter, there is the use of organo-titanium/aluminium species found in the Zeigler-Natta polymerisation of olefins[16]. Fischer-Tropsch synthesis of hydro-carbons has been shown[17] to take place on tungsten/aluminium catalysts.

As homogeneous catalysts the use of organometallics has been legion, and many books have been published devoted to this important area of chemistry. To give three examples, iron and cobalt hydrogen carbonyls[18] have been found to catalyse olefin isomerisation, whilst Wilkinson's catalyst [$RhCl(PPh_3)_3$] catalyses hydrogenation reactions at olefins and acetylenes[19] and the Wacker process, i.e. the oxidation of olefins to aldehydes is catalysed by Pd[20].

The Structure and Reactivity of Organometallic Complexes.

The main factors affecting the structure and reactivity of organometallic complexes have come in for considerable investigation over the years. For instance the trans effect and trans influence[21] and the 18-electron rule, with the importance of 16- and 14-electron species[22] are well understood. The main reaction pathways of ligand substitution[23], oxidative addition/reductive elimination, β-[24] and α-[25] eliminations and insertion reactions[26] have all been described in detail before. There are several textbooks[27-29] that would serve as good introductions to these areas, especially in relation to organoplatinum chemistry. It is not proposed to go into these areas in any more detail here, but rather deal with any of these points as they arise in the text. It is hoped however that the brief introduction has shown why the investigation of organometallic complexes is such an important area of contemporary study.

CHAPTER 2.

SYNTHESES AND LIGAND EXCHANGE REACTIONS OF GOLD(I)ETHYNYLS.

2-1 Introduction.

From pre-historic times right up to the present day, gold, of all the elements, has held the most fascination for man, being widely used in many cultures as a sign of wealth and social status. If the mysterious workings of the alchemists are ignored however, it is only very recently that the chemistry of gold has been investigated, and the majority of that research has been done within the last two decades.

The metal itself is found in the earth's crust at an average concentration of 4 parts per billion. It occurs naturally as the metal either in nuggets or grains after weathering of local rocks, or else in veins in quartz rock. It is extracted by milling the ore to fine particles and then treated with alkaline cyanide and air to dissolve the gold as $[Au(CN)_2]^-$. After filtration, treatment with zinc re-precipitates the metal (eqn 2-1)

$$2[Au(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Au \qquad (2\text{-}1)$$

The gold can be further purified by treatment of the molten crude gold with chlorine gas which removes other metals as their chlorides, leaving gold with a purity of 99.5%. Further refinement can be achieved by electrolysis. Currently the main producers of gold are South Africa and the U.S.S.R., with other African and South American countries producing significant amounts.

Gold is the most noble of all the metals, being the only one which does not react with oxygen or sulphur at any temperature, although

it will combine with tellurium and all the halogens. It will not dissolve in hydrochloric or nitric acids but dissolves readily in aqua regia to produce tetrachloroauric acid, $H[AuCl_4]$, and is commercially available in this form.

There are limited commercial applications of gold and its compounds, apart from the obvious uses for jewellery and monetary standards which do not utilise the chemical properties of the element. Its catalytic properties are very poor[30] due to a completely filled d-band in the metal, so small molecules are chemisorbed only very weakly or not at all. The metal can be used however to modify the catalytic behaviour of other metals[31] such as platinum[32] or rhenium[33]. One of the most rapidly expanding uses of gold is in the electronics industry where, after electroplating onto other materials, it is used in switching devices and for components in micro-electronic circuitry.

There are some biological uses for gold compounds[34] especially in the treatment of arthritis where drugs like Myocrysin[35](Disodium gold thiomalate) and Solganol (gold thioglucose) appear to be as effective as any others in the treatment of this disease. There has also been interest in anti-tumor properties, and some work has been done on gold bases-DNA model systems[36], where gold binds to nitrogen in uracil type bases.

2-2 The Chemistry of Gold

Mononuclear gold complexes are most commonly in the I & III oxidation levels. Gold(II) can be formed if certain bulky unsaturated sulphur ligands are used[37], e.g. gold(II) bis-(maleonitriledithiolate) (fig. 2.1)

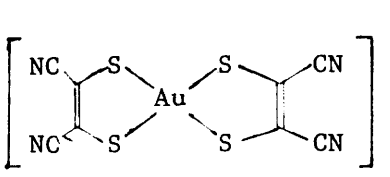


Fig. 2.1

Gold(II) is d^9 and hence paramagnetic, the complexes are stabilised by delocalisation of the unpaired electron over the unsaturated ligands. Diamagnetic gold(II) complexes are formed in dinuclear complexes containing gold-gold bonds e.g. (fig.2.2)[37]

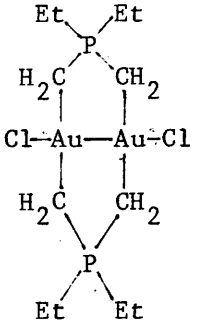


Fig. 2.2

Gold(V) is also well characterised but very rare. $[AuF_6]^-$ was prepared by Bartlett in 1972 and is a good example of fluorine ligands stabilising high oxidation levels. It is a diamagnetic low spin d^6 complex and, not unsurprisingly, a very powerful oxidising agent. This oxidation level has never been isolated in copper or silver complexes.

Other oxidation levels are known for gold. CsAu, a nonmetallic solid containing gold in the -1 oxidation level (the auride ion), was discovered by Sommer in 1943[38]. The ion has also been prepared in liquid ammonia[39] and is the only known example of a transition metal anion in solution.

Fractional oxidation levels of gold also exist in gold cluster

compounds 5,6,8,9,11 and 13 gold atom cores have been discovered in homometallic cluster compounds as well as a giant 55 atom core in $[Au_{55}Cl_6(PPh_3)_2]$[40]. These "unusual" oxidation levels of gold have been the subject of a review article by Schmidbaur and Dash[41].

Gold(I) has the electronic configuration $[Xe].4f^{14}5d^{10}$. The most common stereochemistry of gold(I) complexes is a linear arrangement of two ligands around the gold atom giving 14-electron species. This geometry persists in cationic, neutral and anionic complexes (such as $[Au(PPh_3)_2]^+$, $[AuCl(PPh_3)]$ and $[AuCl_2]^-$). Various theories have been proposed to account for this tendency towards co-ordination of two ligands, a geometry found only rarely in Cu(I) and Ag(I) {although it is very common in Hg(II)-isoelectronic to Au(I)}. Arguments based on electrostatic repulsion and polarising power of the metal cations wrongly predict a close similarity of Ag and Au whereas ligand field theory, which considers the hydridisation of the $(n-1)d_z2$ orbital with the ns and np_z orbital to produce two linear hybrid orbitals (ψ_3 and ψ_4) strongly directed along the z-axis (fig 2-3). The electron pair in $(n-1)d_z2$ will occupy ψ_1 and reduce the repulsion between the electron pair and the ligands. The initial d-s hybridisation will be less favourable as the d-s separation increases. The energy difference between d^9s and

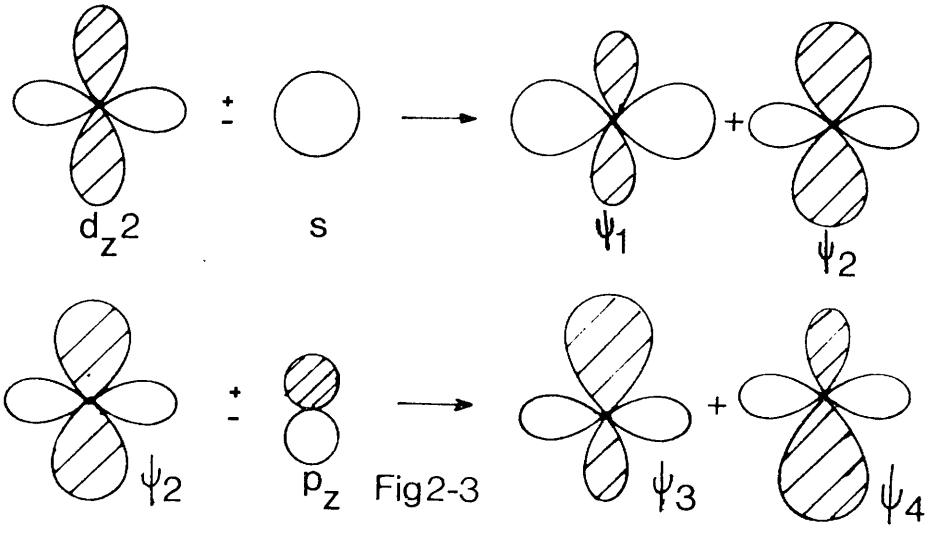


Fig2-3

d^{10} increases in the order $Au^+ < Cu^+ < Ag^+$ which gives the correct series but would predict that copper resembles gold more closely than it does silver, which is not upheld experimentally.

Molecular orbital calculations also predict that linear complexes are favoured for gold and not for copper or silver, since the p orbitals of gold are at relatively high energy and less likely to take part in bonding[42]. So while no one theory produces a result consistent with experimental observation, the trend from all the theories is that the stability of linear complexes decreases in the order Au(I)>>Ag(I)∿Cu(I).

A great number of complexes of the type [AuXL] and [AuRL] (X=halide or pseudo-halide, R=alkyl or aryl, L=donor ligand) are known. The alkyl complexes are prone to decomposition on mild heating in solution (eqn.2-2). The decomposition can also occur

$$2[AuMe(PPh_3)] \rightarrow 2Au + 2PPh_3 + C_2H_6 \qquad (2\text{-}2)$$

photochemically[43] and for $[AuMe(PPh_3)]$ has been shown to produce methyl radicals (eqn.2-3)

$$[AuMe(PPh_3)] \xrightarrow{h\upsilon} [AuMe(PPh_3)]^T \xrightarrow[CDCl_3]{} [AuCl(PPh_3)] + [(Me+CDCl_2)]^T \downarrow$$

variety of products

(2-3)

(T=triplet excited state). Ligand exchange reactions are also well known in the complexes [AuRL] where L can be exchanged without cleavage of the Au-C bond (eqn.2-4)

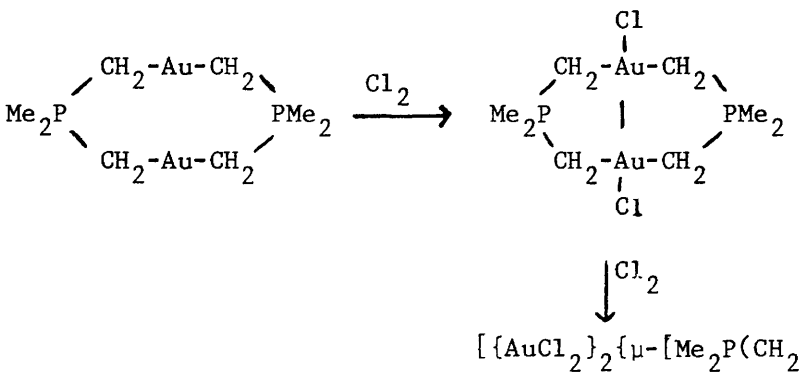
$$[Au(C{\equiv}CPh)(AsEt_3)] + 4\text{-}MeC_6H_4NC \rightarrow [Au(C{\equiv}CPh)(4\text{-}MeC_6H_4NC)] + AsEt_3 \qquad (2\text{-}4)$$

By this and similar reactions the following series of ligands in order of affinity for gold was obtained: phosphine>isonitrile>arsine> stibine>amine[44] and within the phosphines the stability of [AuMeL] was found to be $Ph_3P>Et_3P>Me_3P>(MeO)_3P$.

Gold(I) compounds are also known to undergo oxidative addition reactions to produce gold(III) complexes (eqn.2-5).

$$[AuMe(PPh_3)] + MeI \rightarrow \underline{cis}\text{-}[AuMe_2I(PPh_3)] \qquad (2\text{-}5)$$

With bi-dentate ligands and reduced amounts of oxidising agents the gold(II) intermediates can be isolated[45](eqn.2-6)



(2-6)

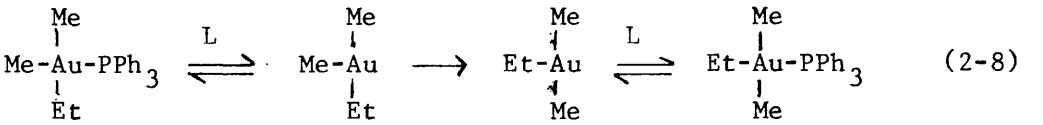
The gold(III) complexes will often undergo reductive elimination back to Au(I) species (eqn.2-7). This reduction was shown specifically to be <u>cis</u> elimination[46] as

$$\underline{cis}\text{-}[AuMe_2I(PPh_3)] \longrightarrow [AuI(PPh_3)] + C_2H_6 \qquad (2\text{-}7)$$

<u>trans</u>-$[AuMe_2Et(PPh_3)]$ will produce only propane and $[AuMe(PPh_3)]$ and no ethane is detected (except under conditions where the $[AuMe(PPh_3)]$ is allowed to decompose (eqn 2-2)).

Gold(III) has electronic configuration $[Xe].4f^{14}.5d^8$ and so is iso-electronic with Pt(II) and like the latter mainly forms 16 electron square planar complexes, although a few five and six co-ordinate structures are known such as $[AuI(diars)_2]^{2+}$ and $[AuI_2(diars)_2]^+$

(diars = 1,2-bis(dimethylarsino)benzene). Like Pt(II) the square planar Au(III) species can exist as different geometrical isomers. Interestingly, whereas 'T' shaped intermediates have been proposed in the isomerisation of $[PtRX(PR'_3)_2]$ [47,48], for certain trialkyl gold(III) decompositions, such intermediates have been proven to exist[46]. So, for example in the isomerisation of cis-$[Au(Et)(Me)_2(PPh_3)]$ the highly reactive $14e^-$ species $[Au(Et)(Me)_2]$ is formed which then can undergo isomerisation[47](eqn 2-8)



(2-8)

2-3 The Chemistry of Gold(I) Ethynyls

Ethynylgold(I) complexes have been known since the beginning of the century, when in 1900 the explosive gold carbide, Au_2C_2, was first reported[50]. More stable ethynylgold complexes are produced when monosubstituted ethynes are used to produce complexes of the form $[Au(C{\equiv}CR)]_n$ [44], which is polymeric when R=Ph, but when R=Bu^t a tetramer is formed (fig.2.4).

More complicated complexes containing only gold with ethynyl ligands can be produced when Au_2C_2 is allowed to react with KC_2H to produce $K[HC{\equiv}C\text{-}Au\text{-}C{\equiv}CH]$ and if the reaction is performed in the presence of acetylene, the bridged anion, $[HC{\equiv}C\text{-}Au\text{-}C{\equiv}C\text{-}Au\text{-}C{\equiv}CH]^-$ [51] is formed. Substituted gold diethynyl anions

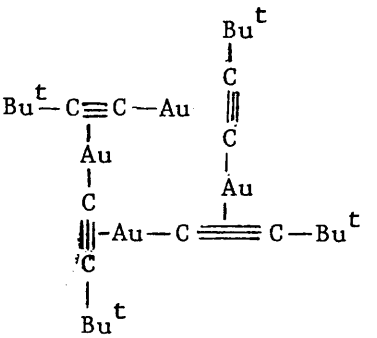


Fig.2.4

e.g. $[Au(C{\equiv}CPh)_2^-]$ [52] will also react further with gold ethynyls to produce larger anions still containing only ethynyl ligands[53] (eqn.2-9)

$$[Au(C{\equiv}CPh)_2]^- + \tfrac{1}{n}[Au(C{\equiv}CPh)]_n \rightarrow \left[\begin{array}{l} Ph \\ | \\ C \\ \equiv \\ C \\ | \\ Au\text{-}Au\text{-}C{\equiv}CPh \\ | \\ C \\ \equiv \\ C \\ | \\ Ph \end{array}\right]^- \qquad (2\text{-}9)$$

and an unusual example of a stable 'T'-shaped Au(I) complex.

Infrared spectroscopy indicates that the gold-ethynyl π-bond is quite weak and it is found that it can be easily cleaved by other donor ligands to produce the complexes $[Au(C{\equiv}CR)L]$[44] ($L=PR_3, AsR_3, NR_3$ SCN). Compared with the alkyl derivatives the ethynyl complexes are very stable, not decomposing thermally or photochemically in solid or solution, and exhibiting much lower chemical reactivity.

As mentioned previously, Au(I) is isoelectronic with Hg(II), and it was thought that it would be interesting to compare the reactions of gold ethynyls with the previously studied mercury ethynyl system[54] in terms of their reactivity towards Pt(II) complexes.

2-4 Results and Discussion

1. Synthesis of $[Au(C{\equiv}CR)L]$ and $[LAuC{\equiv}CAuL]$.

Initial attempts to produce $[Au(C{\equiv}CPh)(PPh_3)]$ followed the method described by Coates and Parkin[44] which involved SO_2 reduction of $HAuCl_4$ in water/acetone to produce "AuCl" followed immediately by $HC{\equiv}CPh$ to form a pale yellow precipitate of $[Au(C{\equiv}CPh)]_n$. Treatment of this solid with Ph_3P is reported to yield $[Au(C{\equiv}CPh)(PPh_3)]$.

However, when attempted it proved extremely difficult to control the SO_2 reduction and little or no $[Au(C{\equiv}CPh)]_n$ was detected. When the brown solid that was produced was treated with Ph_3P, again no gold ethynyl complex was detected.

It was thought that a more convenient and efficient synthesis of gold ethynyls might be found from the phosphine chloro complexes $[AuCl(PR_3)]$. These complexes are well known and easily prepared by reacting $HAuCl_4$ with the phosphine in ethanol[55]. This method was used to prepare samples of $[AuCl(PPh_3)]$, $[AuCl(P\{C_6H_4.CH_3\text{-}p\}_3)]$ and the new complex $[AuCl(P\{C_6H_4OCH_3\text{-}p\}_3)]$, all air stable, white, crystalline solids.

In chloroform solution there was no direct reaction between $[AuCl(PPh_3)]$ and $HC{\equiv}CPh$, and ^{31}P n.m.r. spectroscopy of the product showed only one singlet at δ33.2, identical to the starting chloride complex.

It is known that lithium ethynyls will react with phosphine gold halides[51] to produce the desired species (eqn.2-10) and so the use of bases to promote the

$$[AuBr(PEt_3)] + Li(C{\equiv}CPh) \rightarrow [Au(C{\equiv}CPh)(PEt_3)] + LiBr \qquad (2\text{-}10)$$

reactivity of the very weakly acidic ethyne proton might produce the desired reaction.

When the gold halide complex and phenylacetylene were reacted together in $CHCl_3$ in the presence of Et_3N, an unfavourable reaction between base and solvent prevented the formation of any gold ethynyl. Changing the solvent to benzene stopped the unwanted side reaction, but again no gold ethynyl was produced.

When the synthesis was repeated using diethylamine both as solvent and base the reaction went smoothly at room temperature to

produce [Au(C≡CPh)(PPh_3)] (eqn.2-11). The product was characterised

$$AuCl(PPh_3) + HC{\equiv}CPh \xrightarrow{Et_2NH} [Au(C{\equiv}CPh)(PPh_3)]+[Et_2NH_2]Cl \qquad (2\text{-}11)$$

by the comparison of its infrared spectra and melting points with that of a genuine sample. The reason for the change of reactivity between Et_2NH and Et_3N is unlikely to be due to differing basicities as these are very similar (pK_b=3.07 (Et_2NH) and 3.36(Et_3N)) and probably reflects the fact that Et_2NH is being used in large excess and is a much more polar solvent than those used with Et_3N. It should be noted that platinum ethynyls can be prepared by a similar method (eqn.2-12), although a trace of CuI is required to catalyse the

$$\underline{cis}\text{-}[PtCl_2(PEt_3)_2]+HC{\equiv}CPh \xrightarrow{Et_2NH/CuI} \underline{trans}\text{-}[Pt(C{\equiv}CPh)_2(PEt_3)_2] \qquad (2\text{-}12)$$

reaction[56]. [Cu(C≡CPh)] is proposed as an intermediate in this reaction and (eqn.2-11) shows that ethynyls of group IB metals can be formed from the alkyne and metal halide. This reaction will be discussed more fully in Chapter 3.

The best method found, however, for preparing gold ethynyls involved the use of the strong base Na(OEt) to remove the acidic proton on the alkyne. So when a suspension of [$AuCl(PPh_3)$] in ethanol was treated with freshly prepared sodium ethoxide followed quickly by phenylacetylene, a smooth conversion to [Au(C≡CPh)(PPh_3)] took place (eqn.2-13). The product is very insoluble in EtOH and could be obtained

$$[AuCl(PPh_3)]+HC{\equiv}CPh+NaOEt \rightarrow [Au(C{\equiv}CPh)(PPh_3)]+NaCl+EtOH \qquad (2\text{-}13)$$

nearly pure by filtration. Re-dissolution in $CHCl_3$ and filtration removed the NaCl in the product which could then be re-crystallised by

addition of pentane affording colourless crystals. The melting point and ir parameters (Table 1) are consistent with literature values[44], and ^{31}P n.m.r. spectroscopy showed only one product (δ42.3) which showed no signs of decomposition in solution even after prolonged heating.

When 10% of water was delibrately introduced into the ethanol before reaction, the production of $[Au(C{\equiv}CPh)(PPh_3)]$ still proceeded readily indicating that hydroxide is a strong enough base to promote reaction and small amounts of water in the ethanol will not interfere with the formation of the product. If $[AuCl(PPh_3)]$ and Na(OEt) were mixed in ethanol without the addition of any phenylacetylene no reaction took place and the phosphinegold chloride could be recovered unchanged. Furthermore, addition of excess PhC≡CH to a solution of $[AuCl(PPh_3)]$ did not produce any change in the ^{31}P n.m.r. parameters of the latter, indicating that there is little or no interaction between the two species. This implies that the reaction mechanism does not involve an initial reaction between the gold centre and either the ethoxide or the phenylacetylene and a reaction scheme shown in (eqn.2-14) is thought to

$$\begin{array}{l} HC{\equiv}CPh + EtONa \longrightarrow [PhC{\equiv}C]^- + Na^+ + EtOH \\ \qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow [AuClL] \\ \qquad\qquad\qquad\qquad\qquad [Au(C{\equiv}CPh)L] + Cl^- \end{array} \qquad (2\text{-}14)$$

be the true mechanism for the reaction.

This method proved to be very versatile. $[AuCl(P\{C_6H_4Me\text{-}\underline{p}\}_3)]$ reacts analogously to give $[Au(C{\equiv}CPh)(P\{C_6H_4Me\text{-}\underline{p}\}_3)]$, and by passing gaseous alkynes through suspensions of [AuClL] in ethanolic sodium ethoxide the new compounds [Au(C≡CMe)L], [Au(C≡CEt)L] and $[Au(C{\equiv}CCF_3)L]$ (L=PPh_3) were easily synthesised. The physical and spectroscopic data for these compounds are shown in Table 1.

Physical and Spectroscopic Data for [Au(C≡CR)L]

L	R	M.Pt(°C)	ν(C≡C)(cm^{-1})	δ_P (p.p.m)	δ_H [a] (p.p.m)
PPh_3	H		1,975 [b]	41.9	1.75
	Me	148-150	2,120	41.8	1.98
	Et	154-155	2,115	41.1	1.27(t); 2.40(q).
	CF_3	155	2,128	41.2	
	Ph	163-165 [c]	2,118	42.3	
$P(C_6H_4Me)_3$	Ph	146-148	2,120	40.2	

(a) ^1H data for R groups (b) ν(≡C-H)3,278cm^{-1} (c) Lit[51] 162°C

Table 2-1

If ethyne itself was allowed to react with $[AuCl(PPh_3)]$ in alcoholic Na(OEt), a white insoluble product could be separated. Its ir spectrum showed the acetylene stretch at lower frequency than for the other gold ethynyls and a very strong band at $3278cm^{-1}$. Both these observations are consistent with only one of the ethyne's protons being replaced (similar observations have been seen in compounds containing Pt-C≡CH groups[57]). A singlet in the proton n.m.r. spectrum at δ1.75 is further evidence that the product is $[Au(C{\equiv}CH)(PPh_3)]$ although it proved impossible to purify this compound.

This compound can be thought of as a monosubstituted alkyne and it could be made to react further with more $[AuCl(PPh_3)]$ and base to produce the highly insoluble complex $[(Ph_3P)AuC{\equiv}CAu(PPh_3)]$ (eqn.2-15). Due to its extremely low solubility, this also could not be purified and

$$[AuCl(PPh_3)]+C_2H_2 \xrightarrow{EtONa} [Au(C{\equiv}CH)(PPh_3)] \xrightarrow{[AuCl(PPh_3)]/Na(OEt)} [(Ph_3P)AuC{\equiv}CAu(PPh_3)] \qquad (2\text{-}15)$$

heating in solvents above 60°C led to decomposition. Its identity was inferred from a C≡C stretch at $2040cm^{-1}$ which was Raman active and infrared inactive, which would be expected from a symmetrically substituted alkyne.

Changing the phosphine to either tris-(p-methoxy)phosphine or tris-(p-tolyl)phosphine produced the analagous digold species $[LAuC{\equiv}CAuL]$ (L=tertiary phosphine), although in both these cases the reaction from [AuClL] and ethyne went straight through to the digold products and no $[Au(C{\equiv}CH)L]$ was detected (eqn.2-16). This indicates

$$2[AuClL] + C_2H_2 \xrightarrow{2\ NaOEt} [LAuC{\equiv}CAuL] + 2NaCl \qquad (2\text{-}16)$$

a greater reactivity for $[Au(C{\equiv}CH)L]$ over C_2H_2, and is likely to be due

to the electron withdrawing nature of the metal centre increasing the acidity of the terminal proton. These compounds were much more soluble in alcohol and chlorinated solvents and amenable to purification by crystallisation, and represent the first reported examples of neutral digold(I) species containing a bridging ethynyl.

Re-crystallisation of the complexes from chloroform or dichloromethane led to the well defined solvates $[(\{p\text{-}MeC_6H_4\}_3P)AuC{\equiv}CAu(P\{C_6H_4Me\text{-}p\}_3)]\cdot 3CHCl_3$, $[(\{p\text{-}MeC_6H_4\}_3P)AuC{\equiv}CAu(P\{C_6H_4Me\text{-}p\}_3)]\cdot 2CH_2Cl_2$ and $[(\{p\text{-}MeOC_6H_4\}_3P)AuC{\equiv}CAu(P\{C_6H_4OMe\text{-}p\}_3)]\cdot 2CH_3Cl_3$ (see Table 2 for analysis) when re-crystallised from alcohol, the crystals did not contain solvent molecules (Table 2) and physical data for unsolvated dimers could be measured (Table 3.).

Table 3 Physical Properties of [LAuC≡CAuL]

L	M.Pt(°C)	$\nu(C{\equiv}C)^a(cm^{-1})$	δ_P (p.p.m.)
PPh_3		2040	b
$P(C_6H_4Me\text{-}p)_3$ [d]	110-115	2025	40.7
$P(C_6H_4OMe\text{-}p)_3$	125	c	38.3

a Raman spectra

b Too insoluble in organic solvents

c Strong fluorescence observed

d For tris(chloroform)adduct

The infrared spectra of the adducts also indicated the presence of solvent molecules within the structure. With $CHCl_3$ solvates the ir bands were generally broader, and all the spectra contained a strong band at $\sim 750cm^{-1}$,

Table 2. Microanalytical data for digold complexes{[LAuC≡CAuL](solvent)n}

L	Solvent	n	%C [a]	%H	%Cl	%P
$P(C_6H_4Me\text{-}p)_3$	EtOH	0	50.75(51.47)	4.15(4.13)		4.86(4.47)
	$CHCl_3$	3	40.87(40.76)	3.00(3.28)	22.8(23.02)	
	CH_2Cl_3	2	46.41(46.17)	3.73(3.88)	11.79(11.85)	
$P(C_6H_4OMe\text{-}p)_3$	MeOH	0	47.06(47.07)	3.80(3.77)		5.37(5.52)
	$CHCl_3$	2	40.29(40.58)	3.54(3.26)	14.3(15.62)	4.47(4.55)

[a] calculated value shown in parenthesis.

assigned to υ(C-Cl). This band was absent in those samples re-crystallised from alcohol. The proton n.m.r. of a sample of the chloroform adduct of [LAuC≡CAuL] (L=P(C_6H_4Me-p)$_3$) contained a singlet at δ7.25 due to $CHCl_3$.

On heating at 50°C for 12 hrs. in vacuo it was possible to remove the solvent molecules from the dichloromethane adduct, and from the chloroform adduct of the tris(methoxyphenyl)phosphine complex, but with the trichloroform adduct only partial removal of $CHCl_3$ could be achieved (to form the bis(chloroform)adduct- Found (calc) C,45.2(46.25); H,3.20 (3.71)%). It seems likely that this molecule is acting as a clathrate host, and only the smaller dichloromethane molecules can escape from the structure.

2. Preparation of [Au(C_5H_5)L]

As a further test of the generality of the new synthetic method of gold-carbon bond formation, the reaction of another weakly acidic hydrocarbon, cyclopentadiene was investigated. When allowed to react in a manner exactly analagous to the alkynes, C_5H_6 produced a precipitate of the known[58] complex triphenylphosphinegold cyclopentadienide (eqn.2-17).

$$[AuCl(PPh_3)] + C_5H_6 \xrightarrow{Na(OEt)} [Au(C_5H_5)(PPh_3)] \qquad (2\text{-}17)$$

This represents a better synthetic route than the reported one,[58] which involved reacting [AuCl(PPh_3)] with [Na(C_5H_5)] in $CHCl_3$, as it was found that the product decomposes rapidly (15 mins) in $CHCl_3$ solution, probably by a reaction analagous to(eqn.2-2) as gold mirrors formed on the walls of the reaction vessel. By producing the compound as an insoluble precipitate this problem was solved (although care must be taken as the solid would still decompose slowly in the light).

It was also found that this alkoxide promoted reaction can be further used to prepare ethynyls of Pt(II) (see Chapter 3) and shortly after the initial report on this work[59], Bruce and co-workers published related preparations of ethynyls of gold[60] and other metals such as Ir, Rh, Cu and Ag[61].

3. Ligand Exchange Reactions of Gold Complexes.

(a) Effects of PR_3 on $[AuCl(PR_3)]$

When a 0.1 molar equivalent of Ph_3P was added to a $CDCl_3$ solution of $[AuCl(PPh_3)]$, the initially sharp signal on the ^{31}P n.m.r. spectrum broadened due to a fast exchange of free and co-ordinated phosphine ligands. On cooling to -60°C this exchange was slowed down sufficiently to give sharp bands in the phosphorous spectrum corresponding to $[AuCl(PPh_3)]$ and minor signals at δ41.2 and 31.7 neither of which correspond with free Ph_3P or its oxide, $Ph_3P{=}O$. One of these is likely to be due to the presence of some $[AuCl(PPh_3)_2]$. Although this complex was never isolated in these experiments there are several reports in the literature concerning complexes of the form $[AuXL_n]$ (n=1,2,3) [62], or $[AuL_m]^+$ (m=1,2,3,4)[62a,b,c,e,63] and the systems are very complicated due to the competing equilibria:-

$$[AuL_2Cl] \rightleftharpoons [AuL_2]Cl \qquad (2\text{-}18)$$

$$[AuL_2Cl] \rightleftharpoons [AuClL]+L \qquad (2\text{-}19)$$

It is thought[62c] that (2-19) dominates in less polar solvents, and is displaced in the direction of (2-18) in polar solvents, being quantitative in acetonitrile. Muetterties and Algeranti [62d] reported a further disproportionation reaction (eqn.2-20, $L=[P(C_6H_4Me\text{-}\underline{p})_3]$).

$$2L_2AuCl \rightleftharpoons [AuClL_3] + AuClL \qquad (2\text{-}20)$$

The presence of a multiplicity of signals in the phosphorous n.m.r. has been observed[62f] in the reactions of $[AuBr_2]^-$ with non-chelating bidentate phosphine ligands.

Returning to the reaction in question there are a variety of possibilities for the second minor product and it seems likely to be either $[AuCl(PPh_3)_3]$ or $[Au(PPh_3)_2]^+$.

$[AuCl(P\{\underline{p}\text{-tolyl}\}_3)]$ also underwent rapid phosphine exchange when treated with a trace amount of PPh_3. Low temperature ^{31}P n.m.r. spectroscopy again showed the presence of several species mainly the starting gold chloride as well as signals at δ32.7(due to $[AuCl(PPh_3)]$), and two unknown species at δ42.3 and 31.7 again probably due to bis-(phosphine)gold species being formed.

When one equivalent of PPh_3 was added to either phosphinegold chloride the ^{31}P n.m.r. spectra at low temperature (-60°C) showed several broad peaks in both cases. The low temperature exchange limit could not be reached in $CDCl_3$ and at -60°C several of the possible products must still be undergoing fast exchange.

It is known that elemental sulphur reacts very readily with tertiary phosphines to produce the phosphine sulphides, $R_3P{=}S$, hence free phosphine can be easily and rapidly removed from solution by adding S_8 to the reaction vessel.

When sulphur was added to a solution of $[AuCl(P\{C_6H_4Me\text{-}\underline{p}\}_3)]$ in $CDCl_3$ containing one equivalent of PPh_3, the room temperature ^{31}P n.m.r. spectrum changed from one broad peak to several sharp signals showing the presence of $[AuCl(PPh_3)]$ and $[AuCl(P\{C_6H_4Me\text{-}p\}_3)]$ with other signals at δ43.3 (due to Ph_3PS[64]) and δ42.4 (by analogy assigned to $(\underline{p}\text{-tol})_3PS$) plus two other minor signals at δ31.2 and δ29.5 which have not been assigned. The last two species are unlikely to be $[AuCl(SPR_3)]$ as

independant experiments showed that there was no reaction between $[AuCl(PPh_3)]$ and S_8 or Ph_3PS. The fact that both phosphinegold chlorides are observed clearly indicates that phosphine exchange at gold must be occurring (eqn 2-21).

$$[AuCl(P\{p\text{-tol}\}_3)] + PPh_3 \rightleftharpoons [AuCl(PPh_3)] + P\{p\text{-tol}\}_3 \qquad (2\text{-}21)$$

Further, since the room temperature spectrum of this solution contains only sharp peaks, exchange between the two gold chloride complexes must be very slow.

(b) Phosphine exchange with $[Au(C{\equiv}CPh)L]$

When a 0.1 molar equivalent of Ph_3P was added to solutions containing either $[Au(C{\equiv}CPh)(PPh_3)]$ or $[Au(C{\equiv}CPh)(P\{p\text{-tol}\}_3)]$, the room temperature ^{31}P n.m.r. spectra both contained one broad signal (at δ39.4 and 37.0 respectively) indicative again of rapid phosphine exchange. Unlike the phosphinegold chlorides under similar conditions, cooling to $-60^{o}C$ did not produce significant amounts of line narrowing, indicating that for phosphine *trans* to ethynyls, phosphine exchange is still rapid at low temperature. This can be rationalised as ethynyls are known to have higher *trans* effect than chloride, and the weakening of the Au-P bond would result in more facile ligand exchange.

S_8 was again used to stop the exchange reaction, and addition of S_8 to the sample of $[Au(C{\equiv}CPh)(P\{p\text{-tol}\}_3)]$ + 0.1 Ph_3P produced a room temperature spectrum containing sharp signals assignable to the starting gold ethynyl and $[Au(C{\equiv}CPh)(PPh_3)]$ (ratio 12:1) as well as a minor signal at δ42.6 (due to $(p\text{-tol})_3PS$). Repeating the reaction with double the amount of PPh_3, approximately doubled the amount of triphenylphosphine-gold phenylethynyl (ratio 5.4:1) as expected.

(c) Ligand exchange between gold complexes

When $[AuCl(PPh_3)]$ and $[Au(C{\equiv}CPh)(PPh_3)]$ were mixed together (1:1 mole ratio) in $CDCl_3$, the room temperature ^{31}P n.m.r. spectrum showed only a very slight broadening of the signals due to a slow ligand exchange reaction between the two components. This exchange stopped on cooling and at -60°C, the n.m.r. signals were sharp. On addition of 0.2 molar equivalents of Ph_3P the room temperature signals collapsed into one broad band, approximately midway between the two species (δ36.7), due to phosphine exchange between the two complexes and the free phosphine. Heating the sample to 50°C caused line narrowing due to an increased rate of ligand exchange. Cooling to -60°C caused the signals to separate into signals for the two components, although the slow exchange limit could not be reached and no signal for free Ph_3P was observed.

^{31}P n.m.r. spectroscopy also showed that equilibration between $[AuCl(P\{\underline{p}\text{-tol}\}_3)]$ and $[Au(C{\equiv}CPh)(PPh_3)]$ occurred (eqn.2-22), with all four components being present in nearly equal amounts and the room temperature spectrum exhibited only slight line broadening again indicating that ligand exchange is slow.

$$[AuCl(P\{\underline{p}\text{-tol}\}_3)]+[Au(C{\equiv}CPh)(PPh_3)] \rightleftharpoons [Au(C{\equiv}CPh)(P\{\underline{p}\text{-tol}\}_3)] + [AuCl(PPh_3)] \qquad (2\text{-}22)$$

Clearly this reaction could take place either by exchange of phosphines or else by exchange of ethynyl for chloride. The latter seems likely as:-

(i) A mixture of $[AuCl(PPh_3)]$ and $[AuCl(P\{\underline{p}\text{-tol}\}_3)]$ did not exhibit any exchange whilst a mixture of $[AuCl(PPh_3)]$ and $[Au(C{\equiv}CPh)(PPh_3)]$ did (see above).

(ii) ethynyl for chloride exchange is known to occur between gold and both mercury and platinum (see below).

A third possibility, that of slight decomposition followed by exchange of free and co-ordinated phosphine is highly unlikely as no decomposition of the components in $CDCl_3$ has ever been detected, even on standing for times much longer than that required for equilibrium (2-22) to be established.

(d) Ligand exchange between gold and mercury

When $[Au(C{\equiv}CPh)(PPh_3)]$ was added to a suspension of $HgCl_2$ (2:1 mole ratio) in $CDCl_3$, rapid dissolution of all the solid takes place. ^{31}P n.m.r. spectrscopy indicates the only phosphine containing product is $[AuCl(PPh_3)]$, and no starting ethynyl complex was observed. So the gold must have quantitatively transferred the ethynyl group to mercury (eqn.2-23). If $[AuCl(PPh_3)]$ was treated with either $[Hg(C{\equiv}CPh)_2]$ or $[Hg(C{\equiv}CMe)_2]$ no signal for either gold alkynyl was observed, showing the

$$2[Au(C{\equiv}CPh)(PPh_3)]+HgCl_2 \longrightarrow 2[AuCl(PPh_3)]+Hg(C{\equiv}CPh)_2 \qquad (2\text{-}23)$$

irreversibility of eqn.(2-23).

(e) Ligand exchange between gold and $[PtCl_2L_2]$

Like mercury chloride, platinum(II) chlorides would react with $[Au(C{\equiv}CPh)(PPh_3)]$, with quantitative exchange of ethynyl for chloride and concomitant production of platinum alkynyls. When $[Au(C{\equiv}CPh)(PPh_3)]$ and *cis*-$[PtCl_2(PMePh_2)_2]$ (1:1 mole ratio) were allowed to react a mono-ethynyl platinum complex was produced (eqn. 2-24) whose geometry was

$$[Au(C{\equiv}CPh)(PPh_3)]+\textit{cis}\text{-}[PtCl_2(PMePh_2)_2] \rightarrow [AuCl(PPh_3)]+\textit{trans}\text{-}[PtCl(C{\equiv}CPh)(PMePh_2)_2] \qquad (2\text{-}24)$$

invariably the thermodynamically favoured[65] *trans* form.

With a 2:1 mole ratio of gold ethynyl to platinum dichloride the expected bis(alkynyl) platinum complex was formed (eqn.2-25), but the geometry of the product varies depending on the reaction conditions employed, with trans-form usually formed, but the cis-form observed on rare occasions. (This reaction will be discussed more fully in

$$2[Au(C{\equiv}CPh)(PPh_3)] + \underline{cis}\text{-}[PtCl_2(PMePh_2)_2] \longrightarrow 2[AuCl(PPh_3)] + \underline{cis}\text{- or } \underline{trans}\text{-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] \qquad (2\text{-}25)$$

Chapter 3).

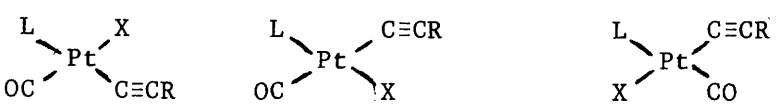
In a similar reaction with $[PtCl_2(PMe_2Ph)_2]$ and phosphinegold alkynyl, the major product was initially cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ with some trans-bis and trans-mono ethynyl complex present, but on standing for 3 days the product had isomerised to produce the trans-bis ethynyl (eqn.2-26)

$$2[Au(C{\equiv}CPh)(PPh_3)] + \underline{cis}\text{-}[PtCl_2(PMe_2Ph)_2] \longrightarrow \underline{cis}\text{-}[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2] \longrightarrow \underline{trans}\text{-}[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2] \qquad (2\text{-}26)$$

The question of the cis → trans isomerisation of the product will also be returned to in Chapter 3.

(f) Reactions of gold phenylethynyls with cis-$[PtCl_2(CO)(PMePh_2)]$

The most interesting of the ligand exchange reactions involved exchange of ligands between gold and (phosphine)(carbonyl) platinum dihalides. There has already been much work performed on the reactions between mercury ethynyls and cis-$[PtCl_2(CO)L]$ (L=$PMePh_2$)[54]. This showed that of the three possible isomers of $[Pt(C{\equiv}CR)Cl(CO)L]$ (see Fig. 2.5) the final product in a 1:1 mole ratio reaction of cis-$[PtCl_2(CO)L]$



(I) (II) (III)

Fig. 2.5

with $[Hg(C{\equiv}CR)_2]$ (R=Me,Ph) is only isomer II, but that the reaction proceeds in a highly stereospecific manner to produce initially isomer I which subsequently reacts as shown in scheme 1. This selectivity of transfer of ethynyl ligand with the chloride trans to a phosphine has been rationalised in terms of the reaction pathway. Ligand exchange between mercury atoms is known to be able to proceed via an S_E2 (cyclic) mechanism[66] (Fig.2.6) and such a mechanism seems likely to apply for exchange between the mercury and platinum atoms. The chloride most likely to participate in such a process would be the one opposite the ligand of highest trans influence, in this case the tertiary phosphine[21a], being the weaker and more polarised of the two Pt-Cl bonds.

It should be pointed out however that a second pathway may operate (see Fig.2.6) involving oxidative addition and reductive elimination of the platinum(II) complex. Such reactions are known to occur for tin and lead complexes with Pt[67]. (A trans oxidative addition could occur only via an ionic mechanism[68] and this seems very unlikely with $[Hg(C{\equiv}CPh)_2]$).

As has already been mentioned, Au(I) is isoelectronic with Hg(II), and it was thought that it would be interesting if the ethynyls of gold display a similar reactivity towards platinum.

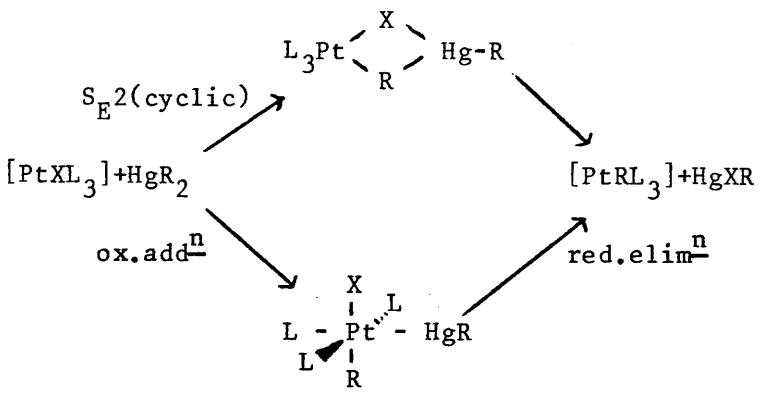
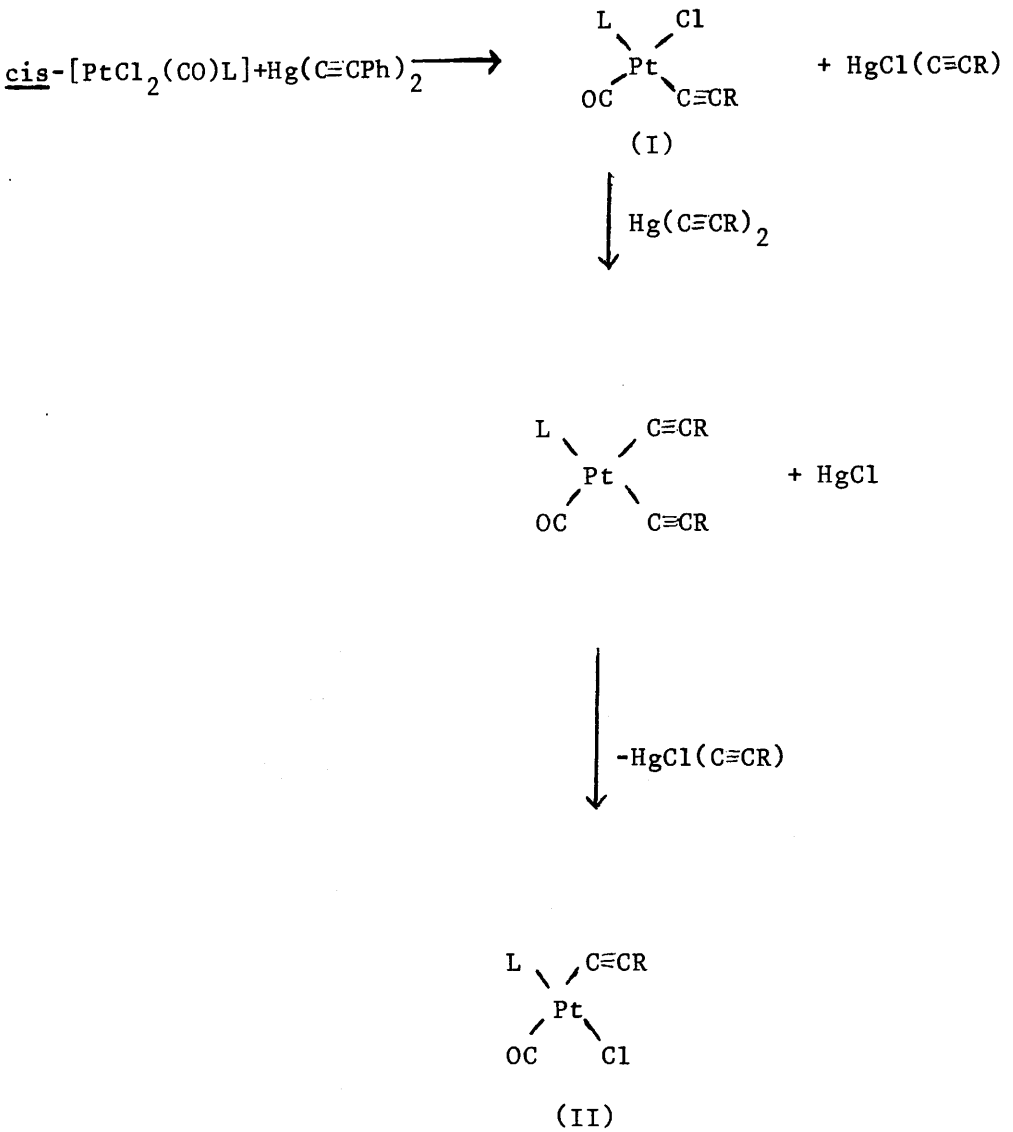


Fig. 2.6


cis-[PtCl2(CO)L]+Hg(C≡CPh)2
L
Cl
Pt
OC
C≡CR
+ HgCl(C≡CR)
(I)
Hg(C≡CR)2
L
C≡CR
Pt
OC
C≡CR
+ HgCl
-HgCl(C≡CR)
L
C≡CR
Pt
OC
Cl
(II)

SCHEME 1.

The reaction of $[Au(C{\equiv}CPh)(PPh_3)]$ with cis-$[PtCl_2(CO)(PMePh_2)]$ was very rapid at room temperature (~5 mins) and like the mercury reactions, the product was isomer II (eqn.2-27) although the appearance

$$\text{cis-}[PtCl_2(CO)(PMePh_2)]+[Au(C{\equiv}CPh)(PPh_3)]\rightarrow[PtCl(C{\equiv}CPh)(CO)(PMePh_2)](II) + [AuClPPh_3] \quad (2\text{-}27)$$

of any intermediates could not be followed due to the rate of reaction. However at -20°C the reaction proceeds at a rate sufficiently slow to follow the reaction course by n.m.r. spectroscopy. The reaction was performed by adding a cooled solution of $[Au(C{\equiv}CPh)(PPh_3)]$ to another cooled solution of cis-$[PtCl_2(CO)(PMePh_2)]$ (1:1 mole ratio, both in $CDCl_3$) and rapid transfer into an n.m.r. sample tube and loading into the spectrometer probe already at -60°C. The ^{31}P n.m.r. spectrum at -60°C showed signals for only the starting materials indicating that no reaction had taken place up to this point. The sample was allowed to heat up to -20°C in the probe, and during this warming period some reaction took place and small amounts of $[PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ isomers I & II (δ2.6 J2027 and δ-4.2 J3183 respectively) were detected, along with a species at δ-6.4 which persisted for a long time, decaying slowly throughout the course of the reaction. After 15 minutes at -20°C a new species was present with parameters δ-2.8 J2087 due to cis-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$[54]. The reaction was monitored at regular intervals over a period of 4 h. and the relative abundance of each species in the reaction mixture is shown graphically in Fig. 2.7. The amount of gold complex has been omitted for clarity, but the gold ethynyl signal decayed, whilst a signal for $[AuCl(PPh_3)]$ grew in until 140 mins, when it was the only phosphinegold complex present. It is at this point the

concentration of the bis-ethynyl complex is at its maximum, and it steadily decreases thereafter. So clearly $[Au(C{\equiv}CPh)(PPh_3)]$ must react preferentially with isomers I and/or II than with $[PtCl_2(CO)(PMePh_2)]$ to produce the bis-ethynyl complex which in turn reacts with cis-$[PtCl_2(CO)(PMePh_2)]$ to produce isomer II, (This last stage has been investigated[69] and these two complexes are known to react in this way). It cannot be said whether both isomers of the mono-ethynyl react with $[Au(C{\equiv}CPh)(PPh_3)]$ to produce the bis-ethynyl complex, but it would seem likely that both do as:-

I) Isomer I appears to be in a "steady state" concentration and so must be reacting as fast as it is produced.

II) In a separate reaction $[Au(C{\equiv}CPh)(PPh_3)]$ and $[PtCl_2(CO)(PMePh_2)]$ (2:1 mole ratio) reacted together to produce only the bis(ethynyl) complex (eqn.2-28).

$$2[Au(C{\equiv}CPh)(PPh_3)]+\text{cis-}[PtCl_2(CO)(PMePh_2)] \longrightarrow \text{cis-}[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]+2[AuCl(PPh_3)] \qquad (2\text{-}28)$$

If either monoethynyl did not react further then it would be left unreacted at the end of this process, which was not observed.

Furthermore from the graph it can be seen that the first reaction step is not stereospecific as isomer II is formed before the bis(ethynyl) complex. Thus the overall pathway can be represented by scheme 2.

Changing the phosphine on the gold atom to $P(\underline{p}\text{-tol})_3$ produced little change in the reaction which proceeded at a very similar rate to produce isomer II. Again the reaction was followed at low temperature ($-20^{o}C$) and the results are shown graphically (Fig.2.8). One notable difference is that even with mixing the components at $-60^{o}C$ some isomer I was identified as well as a quantity of the unknown transient (δ-6.5)

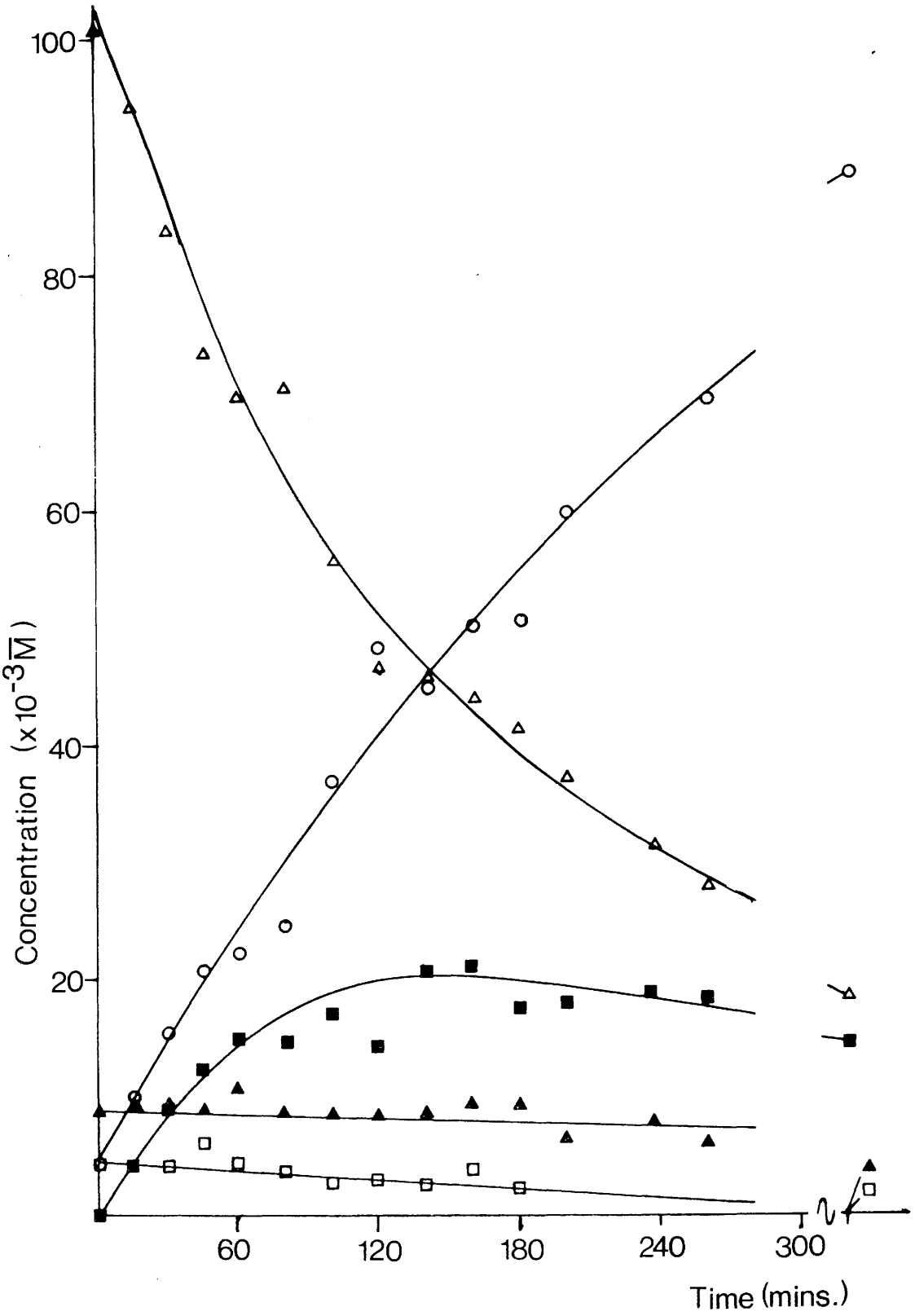


Fig. 2-7 cis-$[PtCl_2(CO)(PMePh_2)]$ + $[Au(C{\equiv}CPh)PPh_3]$ at -20°C

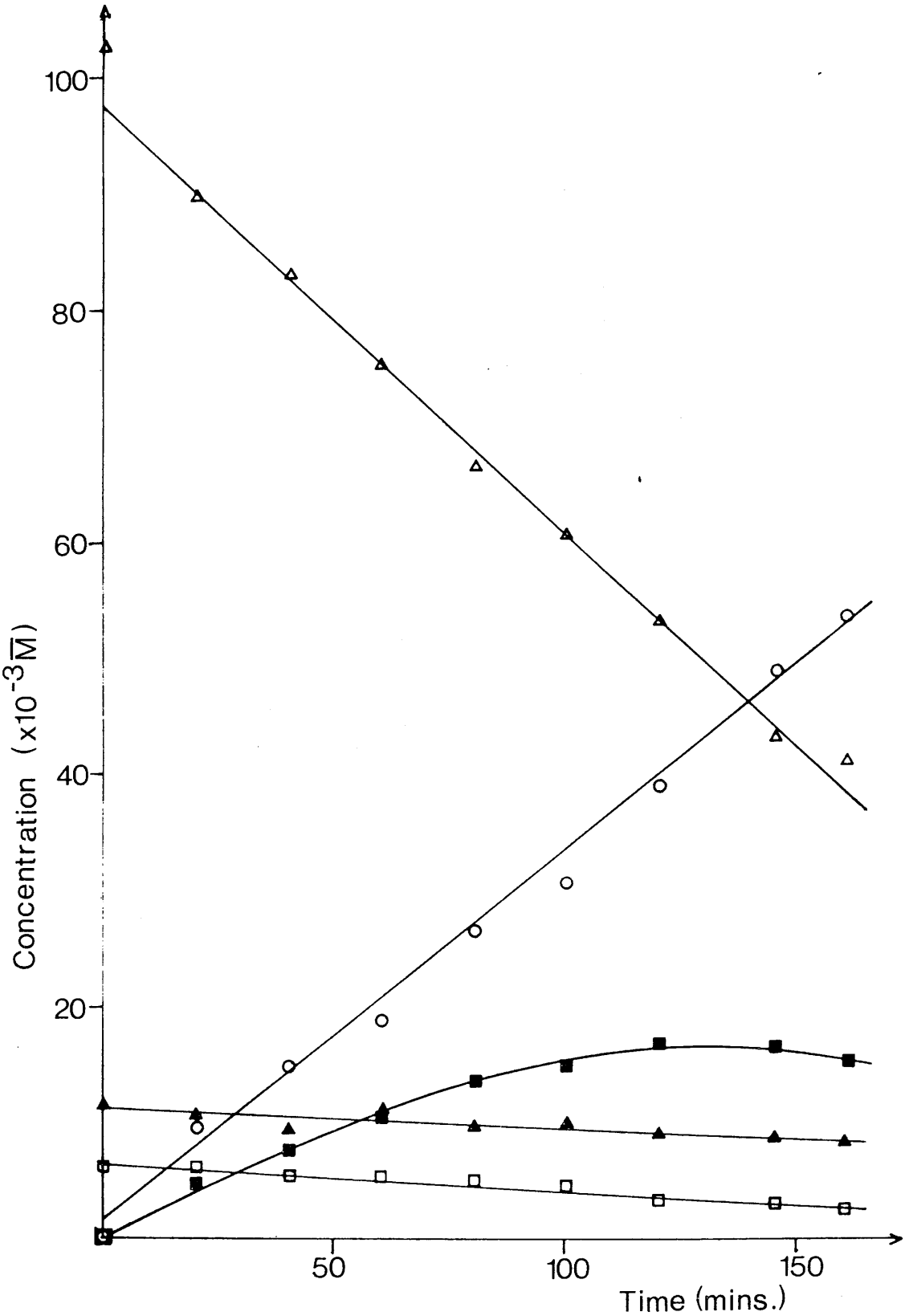


Fig. 2-8 cis-$[PtCl_2(CO)(PMePh_2)]$ +

$[Au(C\equiv CPh)\{P(p\text{-}tol)_3\}]$ at -20°C

Key to Figs. 2-7 and 2-8 :-

△ cis-$[PtCl_2(CO)PMePh_2]$

□ $[PtCl(C{\equiv}CPh)(CO)PMePh_2]$ Isomer I

○ " Isomer II

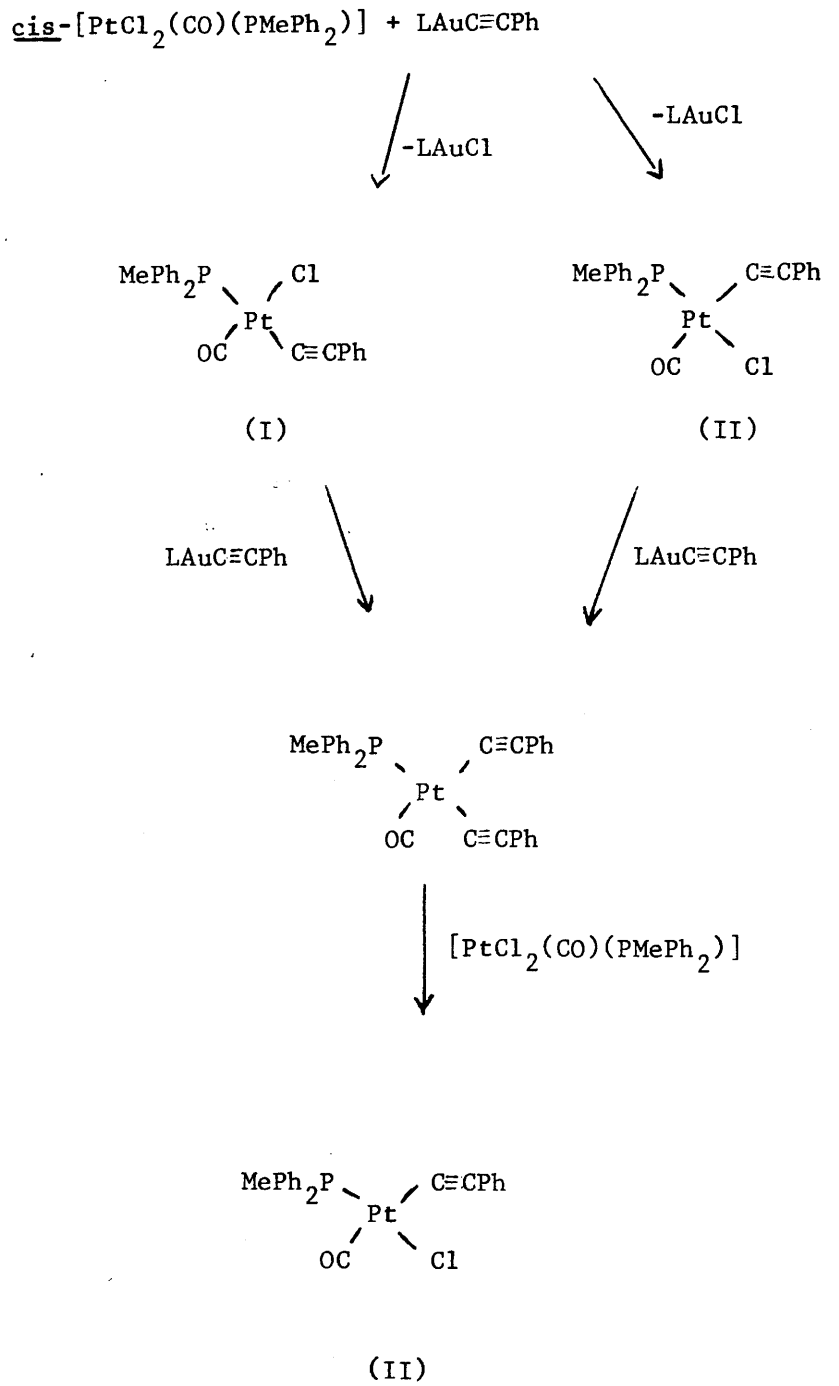
■ cis-$[Pt(C{\equiv}CPh)_2(CO)PMePh_2]$

▲ Unidentified Transient

before any isomer II or bis-ethynyl. On warming again isomer II was detectable before any bis-ethynyl complex, and in all other respects the reaction was analagous to that with $[Au(C{\equiv}CPh)(PPh_3)]$, including consumption of all the gold ethynyl by 150 mins and the reaction follows that shown in scheme 2. The more rapid formation of isomer I over isomer II in this case may indicate that although the fast ethynyl transfer is not stereospecific for gold, there may still be a preference for isomer I.

This lack of stereospecificity is interesting and worthy of comment. Halide replacement by organo groups in $[PtCl_2(CO)L]$ is usually stereospecific[54,69] for alkyls, aryls and ethynyls of mercury, with the first two producing only isomer I and the third producing isomer II via isomer I. Organotin compounds also react to replace the platinum halide with an organogroup[70] and platinum is known to exchange many types of organic group with platinum or palladium including methyl[71], phenyl[72], or cyclopentadienyl[73]. In all cases these exchange reactions are stereospecific. As explained before, the actual mechanism of these reactions is unknown, although in all cases intermediates analagous to those shown in Fig.2.6 have been proposed. It is worthwhile noting that Fig. 2.6 represents the two extremes of a range of transition states depending on how much of the interaction is ascribed to the Pt-Hg bond.

With gold(I), the range of intermediates is extended (Fig.2.7). As well as oxidative addition to platinum, oxidative addition followed by reductive elimination can occur at the gold centre (see eqns. 2-5 to 2-7). This range of transition states is not available to Hg(II) or Sn(IV), as the intermediate oxidation levels Hg(IV) and Sn(VI) are unknown and highly unlikely to be found. Although no S_E2(cyclic) reactions have been proved for Au(I) complexes, there are many examples of oxidative



SCHEME 2. L=Ph_3P, $P(p\text{-}tol)_3$

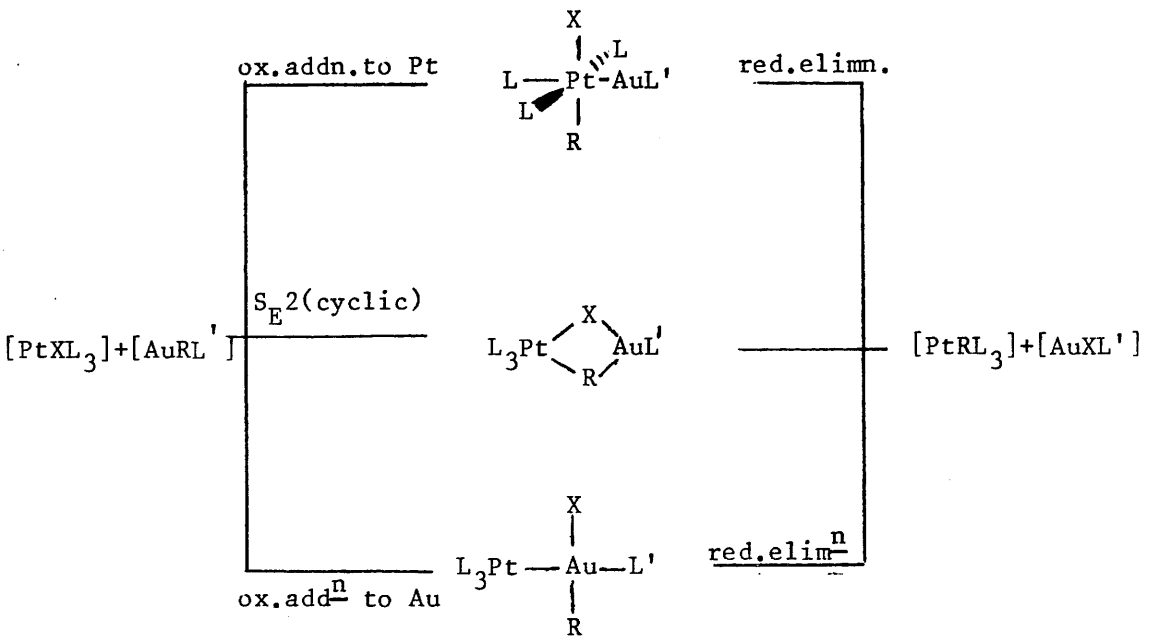


Fig. 2.7

addition/reductive elimination of Au(I) organocompounds and the lack of specificity in ethynyl transfer would indicate either :-

(a) that gold reacts similarly to Hg to produce isomer I whilst a second pathway operates to produce some of isomer II, or

(b) a completely different non stereospecific pathway is operating, which from the results of the reaction with $[Au(C{\equiv}CPh)(P\{p\text{-}tol\}_3)]$ has some selectivity towards isomer I.

In the transfer of ligands between Au(I) and Hg(II) the most probable pathway is the S_E2(cyclic) as found in ligand exchange reactions between mercury atoms[66] and furthermore on S_E2 mechanism has been proven in the methyl exchange from gold to mercury[74].

(g) Reactions of other organogold complexes with cis-$[PtCl_2(CO)(PMePh_2)]$

i) $[Au(C{\equiv}CMe)(PPh_3)]$

The propyne complex $[Au(C{\equiv}CMe)(PPh_3)]$ reacts in an analogous manner to the phenylethynyl complexes to produce $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ isomer II. However the reaction proceeds much more rapidly for propynyl than for phenylethynyl, and even after mixing the reactants at low temperature, the presence of both isomers I & II as well as the bis(propynyl) complex were detected in the phosphorous n.m.r. spectrum at $-60^{o}C$. So it is impossible to gain any information on the stereoselectivity of the first step. It should be noted that this result is consistent with those of mercury alkynyls, where again $[Hg(C{\equiv}CMe)_2]$ was found to react at a far greater rate than $[Hg(C{\equiv}CPh)_2]$[54].

ii) $[Au(C{\equiv}CCF_3)(PPh_3)]$

When two equivalents of $[Au(C{\equiv}CCF_3)(PPh_3)]$ were allowed to react with cis-$[PtCl_2(CO)(PMePh_2)]$ in $CDCl_3$, after a few minutes the ^{31}P n.m.r. spectrum showed the presence of $[AuCl(PPh_3)]$ and one other phosphorus containing species (δ-4.8 J2097 Hz) which is assigned to cis-$[Pt(C{\equiv}CCF_3)_2(CO)(PMePh_2)]$. Under higher resolution, the central signal was shown to be a quartet, due to long range phosphorous-fluorine coupling ($^{5}J_{PF}$1.8Hz) and by analogy to the methylethynyl complex[54], this is likely to be due to the fluorines in the ethynyl cis to the phosphine.

iii) $[Au(C_5H_5)(PPh_3)]$

When the phosphinegold cyclopentadienyl was allowed to react with cis-$[PtCl_2(CO)(PMePh_2)]$, the ^{31}P n.m.r. spectrum showed that the gold had transferred (C_5H_5) quantitatively to platinum to produce isomer I (eqn.2-29). In common with the reactions of $[Hg(C_5H_5)_2]$ and

$$[Au(C_5H_5)(PPh_3)] + \underline{cis}\text{-}[PtCl_2(CO)PMePh_2)] \rightarrow \begin{matrix} & MePh_2P & & Cl & \\ & & \diagdown & \diagup & \\ & & Pt & & \\ & \diagup & & \diagdown & \\ OC & & & & (C_5H_5) \end{matrix} + [AuCl(PPh_3)]$$

(2-29)

$[Tl(C_5H_5)]$[73] this is the only isomer produced, and it should be noted that ethynyls are unusual in forming isomer II. Aryls, alkyls and cyclopentadienyl all form isomer I.

From the above reactions, and the observed fact that mercury will transfer alkynyl groups to Pt (see chapter 3) it is possible to establish an ethynyl transfer sequence of Au(I)>Hg(II)>Pt(II). Similar results have been found for gold-methyl groups which are ruptured by $HgCl_2$[75] and $[PtCl_2(PMe_2Ph)_2]$ [71] although nitro aryl groups were found to transfer from Hg(II) to Au(III)[76] so there is clearly a dependence on oxidation level of the gold centre.

2-5 Conclusions

With the application of the new synthetic method, phosphine gold alkynyls are easy to prepare and present no difficulty in handling or storing. However they seem to have limited potential as reagents in organometallic chemistry due to the similarity of their reactions with the considerably cheaper mercury alkynyls. The lack of stereospecificity in their reactions only further reduces their usefulness. The bridged dimers [LAuC≡CAuL] could be the precursor of some interesting ethynyl bridged bimetallic species of the type $[LAuC{\equiv}CML_n]$ by reacting suitable metal halides with the dimers and may be one possible future use of this class of compound.

2-6 Experimental

I.r. spectra were recorded as KBr discs on a Perkin-Elmer P.E. 580 spectrometer. ^{31}P and ^{1}H n.m.r. spectra were recorded on a Varian XL100 spectrometer (operating in the F.T. mode) and a Perkin-Elmer R32 90MHz spectrometer respectively. Literature methods were employed to prepare [AuClL] (L=PPh_3,P(p-tol)$_3$)[55] and cis-[$PtCl_2(CO)(PMePh_2)$][77].

Chloro[tris(4-methoxyphenyl)phosphinegold]

A solution of $HAuCl_4$ (5g,14.7 mmoles) and (P{C_6H_4OMe-p}$_3$) (5.69g, 16.2 mmoles) in EtOH (100ml) was stirred for 3 hrs at 0°C. A precipitate developed which was filtered giving a yellow solid which proved to be crude [AuCl(P{C_6H_4OMe-p}$_3$)] (5.83g, 68%). Further purification was achieved by re-dissolution into CH_2Cl_2, drying over anhydrous $Mg(SO_4)$ and dropwise addition of diethyl ether until precipitation just began. On standing colourless crystals grew (5.23g, 61%). M.Pt.206-207°C; ν(Au-Cl) 330cm^{-1}; δ_P 29.2 ppm. Analysis: found C,43.2; H3.25, calc. for $C_{21}H_{21}AuClO_3P$ C,43.1; H,3.62%.

Phenylethynyl(triphenylphosphine)gold

(a) By the method of Coates and Parkin[44]

(i) Phenylethynylgold - A solution of gold(III) chloride (2.93g) and KBr (3g) in H_2O (25ml) was diluted with acetone (15ml). SO_2 was bubbled slowly through the solution which turned colourless after a few seconds (lit.prep. reports a yellow solution after several minutes). HC≡CPh (0.52g) in acetone (2ml) was added, followed by Na(CH_3COO) (5g). A black solid formed and was filtered off [1.81g ν(C≡C) 1975cm^{-1}(vw); M.Pt. 105-108°C (dec.). Lit. ν(C≡C) 1975cm^{-1}; M.Pt 105-106°C (dec.)].

(ii) Crude phenylethynyl gold from above (1.3g, 4.4 mmoles) was dissolved in benzene. Ph_3P(1.14g, 4.4 mmoles) was added and the solution stirred for 2 hrs at ambient temperature. Solvent was removed leaving a yellow precipitate which was not [Au(C≡CPh)(PPh_3)] by i.r. analysis.

(b) Via Na(OEt) - To a suspension of [AuCl(PPh_3)] (1g, 2.0mmol) in dry ethanol (400ml) was added Na(OEt) (freshly prepared from Na (48.7mg, 2.1 mmol) in EtOH (5ml) followed immediately by HC≡CPh (208.2mg, 2.0 mmol). The solution was refluxed for 1 hr., cooled and concentrated, after which a white filtrate of crude [Au(C≡CPh)(PPh_3)] was removed by filtration (0.98g, 78%).

(c) Reaction (b) in the presence of H_2O :- The above reaction was repeated, with H_2O being deliberately introduced into the EtOH (10% H_2O by volume) before reaction. I.r. analysis of the product revealed that [Au(C≡CPh)(PPh_3)] had still been produced (75% yield).

(d) Reaction in Et_2NH solution :- To a suspension of [AuCl(PPh_3)] (100mg, 0.20 mmol) in Et_2NH (30ml) was added HC≡CPh (20.6mg, 0.20 mmol). The mixture was stirred for 3hrs during which time most of the solid had dissolved. The solution was filtered, solvent removed and the Et_2NH soluble product re-crystallised from toluene/methylcyclohexane to produce pure [Au(C≡CPh)(PPh_3)] (68.3mg, 60%)(confirmed by ir spectrum and melting point).

Reaction between [AuCl(PPh_3) and NaOEt :- When Na(OEt) (from 14mg, 0.61 mmol Na) was added to a suspension of [AuCl(PPh_3)] (200mg, 0.4 mmol) in EtOH (50ml) no reaction took place at room temperature or in boiling solvent and the starting phosphinegold chloride was recovered unchanged.

Methylethynyl(triphenylphosphine)gold :- Propyne was slowly passed through a suspension of [AuCl(PPh_3)] (0.5g, 1.0mmol) in EtOH (25ml) to which Na(OEt) (from 43.2mg, 1.9mmol Na) had been added. The solution was kept at 60°C for 1 hr during which time the solid thinned and reformed. The solution was cooled and concentrated. Crude [Au(C≡CMe)(PPh_3)] was filtered off and re-crystallised from $CHCl_3$/pentane to produce colourless crystals (0.28g, 56%) Found C,50.35; H4.4 Calc for $C_{21}H_{18}AuP$, C,50.6; H,3.6%.

1-Butynyl(triphenylphosphine)gold :- This was prepared analogously from but-1-yne at room temperature. Pure product crystallised directly from the reaction solution. Yield 63%. Found C,51.5; H,3.75, Calc. for $C_{22}H_{20}AuP$ C,51.6; H3.9%.

Trifluoromethylethynyl(triphenylphosphine)gold :- Again prepared analogously to [Au(C≡CMe)(PPh_3)] from [AuCl(PPh_3)] (500mg, 1.0mmol) and $HC{\equiv}CCF_3$ at 0°C. [Au(C≡CCF_3)(PPh_3)] crystallised directly from the reaction mixture. Yield 246mg (44%). Found: C,45.5; H,2.6 Calc. for $C_{21}H_{15}AuF_3P$: C,45.7; H,2.7%.

Ethynyl(triphenylphosphine)gold :- C_2H_2 was passed through a suspension of [AuCl(PPh_3)] containing one equivalent of Na(OEt), and the mixture stirred for 1 hr. at room temperature. No reaction appeared to occur and the white solid filtered off. Ir and n.m.r. parameters were consistent with [Au(C≡CH)(PPh_3)] (Table 1). The product could not be purified despite several attempts at re-crystallisation from various organic solvents.

μ-Ethynylene-bis[triphenylphosphine]gold :- Impure [Au(C≡CH)-(PPh_3)] (0.38g, 0.74 mmol) was added to a suspension of [AuCl(PPh_3)]

(0.36g, 0.73 mmol) containing one equivalent of Na(OEt) (from 17mg Na) and the mixture stirred for 1 hr at room temperature. A white precipitate of $[(Ph_3P)AuC{\equiv}CAu(PPh_3)]$ (0.66g, 95%) was removed by filtration. The complex was highly insoluble in all common organic solvents, and decomposed at temperatures >60°C, so purification was not achieved.

μ-Ethynylene-bis[tris(p-tolyl)phosphinegold] :- Passing C_2H_2 through a suspension of $[AuCl(P\{p\text{-}tol\}_3)]$ (1.0g, 1.9 mmol) in ethanol (50ml) containing Na(OEt) (from Na (43.7mg, 1.9mmol) on EtOH) for 45 mins. caused dissolution of the starting material and appearance of a white solid. Filtering produced crude product (490mg). Found C,50.7; H,4.2 Calc. for $C_{44}H_{42}Au_2P_2$: C,51.7; H,4.1%. Re-crystallisation from CH_2Cl_2 or $CHCl_3$/pentane produced the bis(dichloromethane) and tris(chloroform) solvates respectively. (See Table 2). CH_2Cl_2 could be removed from its adduct by heating to 50°C in vacuo for 12 hrs., but chloroform could not be removed completely under similar conditions.

μ-Ethynylene-bis[tris(4-methoxyphenyl)phosphinegold] :- This was similarly prepared by passing C_2H_2 through a suspension of $[AuCl(P\{C_6H_4\text{-}OMe\text{-}p\}_3)]$ (4.5g, 7.7 mmol) in EtOH (100ml) containing Na(OEt) (from Na (177mg, 7.7 mmol) in EtOH) and stirring at 0°C for 1 hr. The solvent was reduced and a white solid of crude product removed by filtration (2.7g, 63%). Re-crystallisation from MeOH gave pure $[(\{MeOC_6H_4\}_3P)AuC{\equiv}CAu(P\{C_6H_4OMe\}_3)]$, as colourless crystals (see Tables 2 and 3). Re-crystallisation from $CHCl_3$ gave the bis(chloroform)adduct.

Cyclopentadienyl(triphenylphosphine)gold :-

(a) Modified Method of Huttel[58]. $[AuCl(PPh_3)]$ (20mg, 40μmol) was dissolved in $CDCl_3$. $Tl(C_5H_5)$ (10.8mg, 40μmol) was added and the

solution shaken for 10 mins, followed by filtration to remove unwanted thallium salts. ^{1}H n.m.r. spectroscopy indicated that the desired product had been formed ($\delta(C_5H_5)6.2(s)$) but on standing at room temperature (15 mins) extensive decomposition took place with a gold mirror forming on the walls of the sample tube.

(b) Via Na(OEt) - To $[AuCl(PPh_3)]$ (500mg, 1.0mmol) suspended in EtOH(50ml) was added Na(OEt) (23.2mg, 1.0mmol Na in 2ml EtOH), followed by freshly cracked C_5H_6 (66.5mg, 1.0mmol). The solution was stirred for 1 hr at ambient temperature, and on standing overnight at $0^{o}C$ a pale yellow precipitate of $[Au(C_5H_5)(PPh_3)]$ formed (404mg, 76%). Proton n.m.r. and i.r. parameters agree with literature values[58] δ_P 36.4 p.p.m. The solid is light sensitive and so was stored in the dark at $5^{o}C$.

PHOSPHINE EXCHANGE REACTIONS

These were all performed on a small scale and the reactions followed by ^{31}P n.m.r. spectroscopy.

$[Au(C{\equiv}CPh)(PPh_3)]+0.1PPh_3$ - on addition of the phosphine a broad signal was detected (δ_P 39.4). Cooling to $-60^{o}C$ caused a slight change in chemical shift (to δ41.6) with no appreciable narrowing indicating a fast exchange of phosphine at both temperatures.

$[Au(C{\equiv}CPh)(P\{p\text{-}tol\}_3)]+0.1PPh_3$ - again both room and low ($-60^{o}C$) temperature spectra indicated fast exchange of phosphine with only broad signals being observed (δ37.0 and δ39.7 respectively).

On addition of excess S_8, followed by filtration both room and low temperature spectra showed sharp resonances due to $[Au(C{\equiv}CPh)(P\{p\text{-}tol\}_3)]$ (δ40.2 at $-60^{o}C$) and $[Au(C{\equiv}CPh)(PPh_3)]$ (δ42.4) (ratio 12:1)

and a minor signal due to $(p\text{-tol})_3PS$ (δ42.6).

$[AuCl(PPh_3)]+0.1PPh_3$ - At room temperature the spectrum showed one broad signal (δ33.7). Cooling to -60°C produced a sharpening of this signal with minor resonances at δ41.2 and δ31.7. These have not been assigned but are probably due to excess phosphine co-ordination to give $[AuCl(PPh_3)_n]$ (n = 2,3) or products from the reactions of these species.

$[AuCl(PPh_3)]+1.0PPh_3$ - At room temperature one sharp band was observed (δ30.2), probably due to $[AuCl(PPh_3)_2]$. On cooling to -60°C, two broadened peaks appeared (δ41.9, 32.8) with one sharp signal (δ31.7). The broad signals may be due to $[AuCl(PPh_3)_3]$ and products from its reactions, whilst the sharp resonance may correspond to $[AuCl(PPh_3)_2]$, and be the same species as was observed in the preceding reaction.

$[AuCl(P\{p\text{-tol}\}_3)]+0.1PPh_3$ - The room temperature spectrum showed one broad signal (δ31.8). At -60°C, sharp resonances were observed at δ30.7 $[AuCl(P\{p\text{-tol}\}_3)]$ and δ32.7 $[AuCl(PPh_3)]$ (ratio 14:1) with minor resonances at δ42.3 and 31.7

$[AuCl(P\{p\text{-tol}\}_3)]+1.0PPh_3$ - At room temperature there were two sharp signals at δ33.8 and 30.1. On cooling at -60°C considerable broadening occurred with broad bands at δ42.1, 32.1, 30.7 and one sharp signal at δ31.8.

$[AuCl(PPh_3)]+[Au(C\equiv CPh)(PPh_3)]$ - When equimolar amounts of these complexes were mixed in $CDCl_3$, two bands showing only slight broadening were observed in the ^{31}P n.m.r. spectrum (δ32.7 and 41.2 for chloride and alkynyl respectively). On addition of 0.2 equivalents of PPh_3, the spectrum collapsed into one broad signal (δ37.0) which

sharpened on warming to 50°C, but on cooling to -60°C separated into two signals for the starting complexes, which still showed signs of exchange.

OTHER LIGAND EXCHANGE REACTIONS

$[AuCl(P\{p\text{-}tol\}_3)]+[Au(C{\equiv}CPh)(PPh_3)]$ - A $CDCl_3$ solution of equimolar amounts of these species showed four signals of nearly equal intensity corresponding to the starting materials, $[AuCl(PPh_3)]$ and $[Au(C{\equiv}CPh)(P\{p\text{-}tol\}_3)]$.

$2[Au(C{\equiv}CPh)(PPh_3)]+HgCl_2$ - When $[Au(C{\equiv}CPh)(PPh_3)]$ (73μmol) was added to a suspension of $HgCl_2$ (37μmol) in $CDCl_3$, the solid dissolved and the ^{31}P n.m.r. spectrum showed only the presence of $[AuCl(PPh_3)]$ (δ32.8). The other product must be $[Hg(C{\equiv}CPh)_2]$

$[Au(C{\equiv}CPh)(PPh_3)+$*cis*$-[PtCl_2(CO)(PMePh_2)]$ - Separate samples of $[Au(C{\equiv}CPh)(PPh_3)]$ (33.9mg, 60.5μmol) and *cis*-$[PtCl_2(CO)(PMePh_2)]$ (29.9mg, 60.5μmol) were dissolved in minimum amounts of $CDCl_3$ and both cooled to -60°C, with the platinum complex already loaded into an n.m.r. sample tube. The sample of phosphine gold alkynyl was rapidly transferred into the tube. ^{31}P n.m.r. spectroscopy at -60°C indicated that no reaction had occurred during trasnfer. The sample was allowed to warm to -20°C in the spectrometer probe. 10 minutes was allowed for warming to be complete, then the reaction was monitored by ^{31}P n.m.r. spectroscopy.

$[Au(C{\equiv}CPh)(P\{p\text{-}tol\}_3)]+$*cis*$-[PtCl_2(CO)(PMePh_2)]$ - This reaction was performed analagously to the preceding one, and produced identical results except that during mixing of the two starting compounds, some reaction took place to produce isomer I(δ0.2, J2945) and an unidentified transient(δ-6.5) possibly due to slight warming of the sample during transfer into the n.m.r. spectrometer probe.

$[Au(C{\equiv}CMe)(PPh_3)]$+cis-$[PtCl_2(CO)(PMePh_2)]$ - Again the reaction was performed analagously to the two above, except in this case the presence of isomers I & II and cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ were detected on mixing. The final product was $[Pt(C{\equiv}CMe)Cl(CO)(PMePh_2)]$ isomer II.

$2[Au(C{\equiv}CCF_3)(PPh_3)]$+cis-$[PtCl_2(CO)(PMePh_2)]$ - The two complexes were allowed to react in $CDCl_3$ to produce two compounds, as detected by ^{31}P n.m.r. spectroscopy, $[AuCl(PPh_3)]$ (δ31.7) and a new species (δ-4.8 J 2097 $^5J_{PF}$ 1.8Hz) assigned to cis-$[Pt(C{\equiv}CCF_3)_2(CO)(PMePh_2)]$.

$[Au(C_5H_5(PPh_3)]$+cis-$[PtCl_2(CO)(PMePh_2)]$ - when allowed to react at room temperature, the complex rapidly produced $[AuCl(PPh_3)]$ and $[Pt(C_5H_5)Cl(CO)(PMePh_2)]$[73].

CHAPTER 3.

THE FORMATION AND ISOMERISATION OF PLATINUM BIS-ETHYNYL COMPLEXES.

3.1 Introduction

The study of organocompounds of platinum, as already mentioned in Chapter 1 has been a very large area of investigation. The metal forms Pt-C σ-bonds in oxidation levels (0), (I),(II),(III) and (IV). The ethynyl complexes have been of particular interest, as they possess higher stability than alkyls and non-ortho-substituted aryls in terms of resistance to aerial oxidation, hydrolysis and thermal decomposition. (For ortho-substituted aryls, the o-group hinders nucleophilic attack at the Pt atom [78] and increases the kinetic stability of the complexes[15] (Fig 3-1, L = PEt_3)

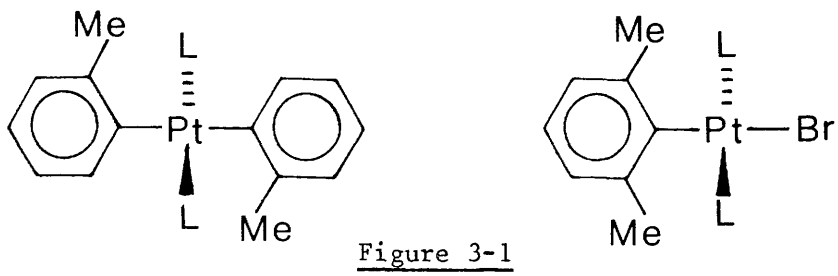


Figure 3-1

The higher stability is reflected in the nature of the Pt-C bond. All three types of ligand (alkyl, aryl and ethynyl) have a σ component from the filled sp^3, sp^2 or sp hybrid orbital on carbon to a platinum hybrid orbital. However the amount of π-back bonding, which would increase the strength of the Pt-C bond, varies. For methyl; there was originally thought to be no back donation as the orbitals on carbon are fully involved in bonding to the three hydrogen atoms. NMR evidence[79] suggests however that some π-back donation does occur. With aryl components the π-bonding component can be"both ways" with filled π-orbitals on the aryl interacting with empty hybrid

orbitals on Pt, as well as the normal filled metal orbitals interacting with π^* orbitals on the ligand.

In platinum ethynyls, the bonding is similar to that found in the neutral isoelectric ligands CO and CNR with a σ component from the filled sp hybrid on carbon and back donation into empty π^* orbitals as shown in Fig 3-2.

3.2 Reactions of Platinum Ethynyls.

There have been many uses of platinum ethynyls in the literature. They can react at the metal centre (like any organoplatinum) or else at the triple bond depending upon reaction conditions.

(i) Carbene Formation - One of the most studied reactions has been acid attack at the triple bond. In protic solvents, such as alcohols, carbene formation is observed (eqn. 3.2; Fc = ferrocenyl)[80]

$$\underline{trans}\text{-}[Pt(C{\equiv}CF)Cl(PMe_2Ph)_2] + HPF_6 \xrightarrow{MeOH} \underline{trans}\text{-}[PtCl\{C(OMe)CH_2F\}(PMe_2Ph)_2][PF_6] \quad (3.2)$$

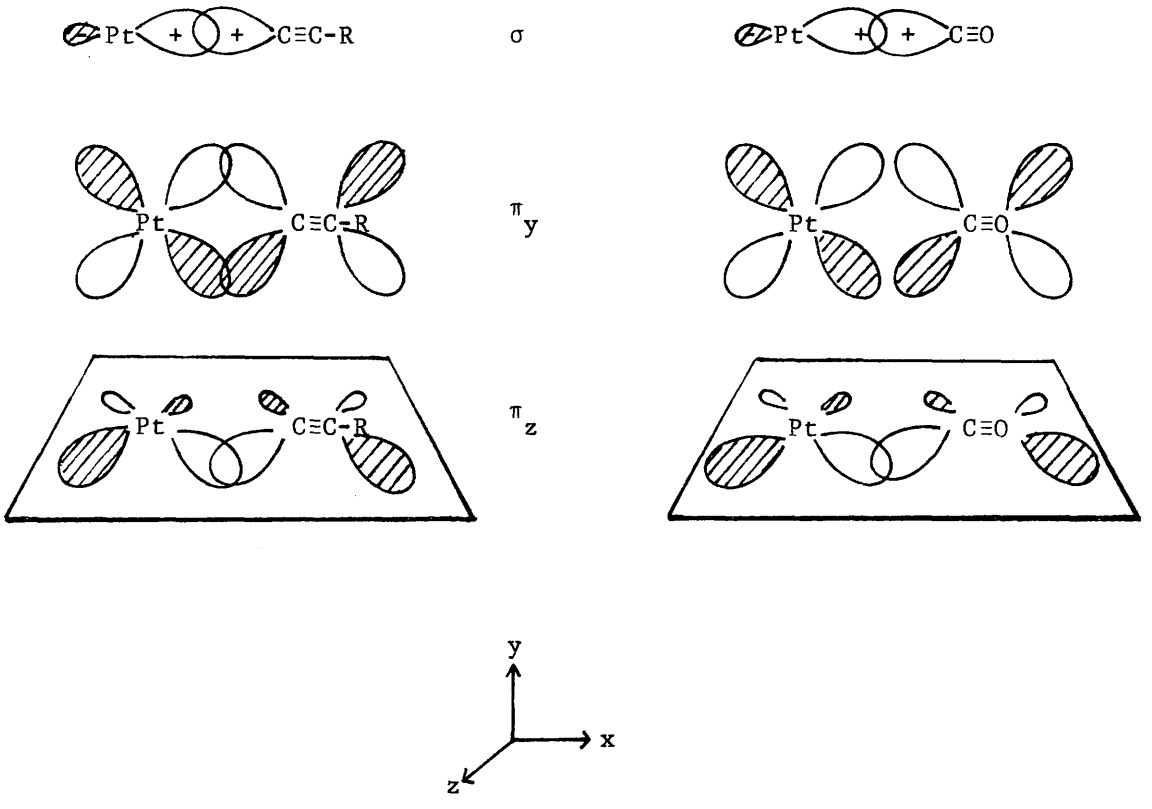
With bis(ethynyl) complexes only the mono carbene is produced[57] (eqn. 3.3). If HCl is used the carbene will react further to produce the acyl complex (eqn. 3.4). (The formation of carbenes from ethynyls shall be discussed more fully in Chapter 4.

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)_2(PMe_2Ph)_2] + HPF_6 \xrightarrow{ROH} \underline{trans}\text{-}[Pt(C{\equiv}CMe)\{C(OR)C_2H_5\}(PMe_2Ph)_2]^+[PF_6]^- \quad (3.3)$$

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)Cl(PMe_2Ph)_2] + HCl \xrightarrow{MeOH} \underline{trans}\text{-}[Pt\{C(OMe)C_2H_5\}Cl(PMe_2Ph)_2]^+Cl^- \longrightarrow \underline{trans}\text{-}[Pt(COC_2H_5)Cl(PMe_2Ph)_2] + MeCl \quad (3.4)$$

Figure 3.2 Bonding of alkynyls and CO to Pt.

(ligand is on the x axis)



(ii) Vinyl Derivatives - With trifluoromethylethynyl platinum complexes however the above reactions do not give carbenes. HPF_6 has no effect and HCl in methanol only adds across the triple bond to give a vinyl derivative[51] (eqn. 3.5). Similar reduction to

$$\underline{trans}\text{-}[Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2]+2HCl \xrightarrow{MeOH} \underline{trans}\text{-}[Pt(CCl{=}CHCF_3)_2(PMe_2Ph)_2] \quad (3.5)$$

σ-bonded vinyl species can be achieved by HCl attack on the triple bond in aprotic solvents with $Pt\text{-}C{\equiv}CCH_2OMe$ groups[81] (eqn. 3.6), although the reaction is accompanied by cleavage of one of the ethynyl groups as $HC{\equiv}CR$. With $C{\equiv}CCMe_2OH$ the reaction is further complicated

$$\underline{trans}\text{-}[Pt(C{\equiv}CCH_2OMe)_2(PMe_2Ph)_2]+2HCl \longrightarrow \underline{trans}\text{-}[Pt\{CCl{=}CH.CH_2OMe\}\,Cl(PMe_2Ph)_2] \quad (3.6)$$

$$\underline{trans}\text{-}[Pt\{C{\equiv}CC(Me)_2OH\}_2(PMe_2Ph)_2]+2HCl \rightarrow \underline{trans}\text{-}[Pt\{CCl{=}CHC(Me){=}CH_2\}Cl(PMe_2Ph)_2] \quad (3.7)$$

by spontaneous dehydration[81] (eqn. 3.7). With the simpler ethynyls $C{\equiv}CMe$ and $C{\equiv}CH$, one or both ethynyls are cleaved[82][83](eqns. 3.8, 3.9),

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)_2(PMe_2Ph)_2]+2HCl \longrightarrow \underline{cis}\text{-}[PtCl_2(PMe_2Ph)_2]+2MeC{\equiv}CH \quad (3.8)$$

$$\underline{trans}\text{-}[Pt(C{\equiv}CH)_2(PMe_2Ph)_2]+HCl \longrightarrow \underline{trans}\text{-}[Pt(C{\equiv}CH)Cl(PMe_2Ph)_2]+HC{\equiv}CH \quad (3.9)$$

the latter follows a complicated pathway via HCl addition across the triple bond.

The reduction of ethynyl to vinyl ligands can also be achieved by treatment of the complexes by hydrazine hydrate[81], with two hydrogens adding <u>cis</u> across the triple bond (eqn. 3.10).

$$\underline{trans}\text{-}[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]+H_4N_2 \rightarrow \underline{trans}\text{-}[Pt(CH{=}CHR\text{-}\underline{cis})_2(PMe_2Ph)_2] \quad (3.10)$$

CF_3COCl, Br_2 and NOCl all add similarly across the triple bond to give vinyl derivatives[84] (eqn. 3.11)

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)_2(PMe_2Ph)_2]+2CF_3COCl \rightarrow \underline{trans}\text{-}[Pt(CCl{=}C(Me)COCF_3)_2(PMe_2Ph)_2] \quad (3.11)$$

(iii) Cyclisation Reactions - If, by use of chelating diphosphines a cis-bis(ethynyl) complex is prepared then treatment with a Lewis acid can cause cyclisation to an unsaturated metallocyde[85] (eqn 3.12, R = Me, Et, Pr)

$$(dppe)\,Pt(C{\equiv}CH)_2+BR_3 \longrightarrow (dppe)Pt\langle \rangle^{R}_{BR_2} \quad (3.12)$$

(iv) Oxidative Addition - trans-$[Pt(C{\equiv}CR)XL_2]$ will undergo oxidative addition but the rate depends on L,X and R in the order L = $AsMe_3$>PMe_2Ph ; X = C≡CR>Cl ; R = Me>H>Ph. the substrate can be I_2, CF_3I, MeI, IBr (but not Br_2 or NOCl - see (ii) above) and the reactions produce the expected Pt(IV) species[84] (eqn. 3.13)

$$\underline{trans}\text{-}[PtX(C{\equiv}CR)L_2]+ A\text{-}B \longrightarrow \underline{trans}\text{-}[Pt(C{\equiv}CR)X(A)(B)L_2] \quad (3.13)$$

LiR (R=Bu^n,Ph) can also add oxidatively to Pt(II) complexes producing unusual Li-bridged dimers[86] (eqn. 3.14)

$$\underline{trans}\text{-}[Pt(C{\equiv}CR')_2L_2]+LiR \longrightarrow \text{L-Pt-R(C≡CR)(Li)R-Pt-L} \quad (3.14)$$

(v) Insertion Reactions and Adduct Formation.

Only one example of insertion into a platinum ethynyl bond in neutral complexes is known (eqn. 3.15) that of tetracyanoethylene[84] although allene insertion into cationic ethynyl complexes is also known (eqn. 3.16).

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)_2(AsMe_3)_2]+(NC)_2C{=}C(CN)_2 \longrightarrow \underline{trans}\text{-}[Pt\{C(CN)_2C(CN)_2C{=}CMe\}_2(AsMe_3)_2] \quad (3.15)$$

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)\{OC(CH_3)_2\}(PMe_2Ph)_2]^+ + CH_2{=}C{=}CH_2 \longrightarrow [Pt\{(CH_2)_2C\text{-}C{\equiv}Me\}(PMe_2Ph)_2]^+ \quad (3.16)$$

Hexafluoroacetone will react with ethynyls by inserting into the C-H bond, generating a new ethynyl complex (eqn. 3.17) [84]. When substituted ethynyls are used, stable π-complexes

$$\underline{trans}\text{-}[Pt(C{\equiv}CH)_2(PMe_2Ph)_2]+2(CF_3)_2CO \longrightarrow \underline{trans}\text{-}[Pt\{C{\equiv}C.C(OH)(CF_3)_2\}(PMe_2Ph)_2] \quad (3.17)$$

are formed instead (eqn. 3.18, X=C≡CMe,Cl)[84], although with trifluoromethylethynyls, the extreme electron

$$\underline{trans}\text{-}[Pt(C{\equiv}CMe)X(AsMe_3)_2]+(CF_3)_2CO \longrightarrow \begin{matrix} & & AsMe_3 & & \\ & X & | & O & \\ & \diagdown & Pt & \diagup & \\ MeC{\equiv}C & & | & & C(CF_3)_2 \\ & & AsMe_3 & & \end{matrix} \quad (3.18)$$

withdrawing nature of the ligand presents such a reaction as there is insufficient electron density at the Pt centre to form π-bonds to the hexafluoroacetone. Other unsaturated ligands (e.g. O_2, allene, CO_2, SO_2, CF_3CN) do not form adducts with even the hydrocarbon substituted ethynyl complexes.

3.3 Preparation of Pt Ethynyls

As a consequence of both the high stability of platinum ethynyls and the high degree of interest expressed in such compounds, there has

been an overwhelming number of preparative routes devised for their synthesis, especially for the phosphine complexes $[Pt(C{\equiv}CR)_2L_2]$ and $[Pt(C{\equiv}CR)XL_2]$.

The original preparation of platinum ethynyls involved the use of Grignard reagents[15,87] organolithium[88] and organosodium[89,80,15] derivatives have also proven very successful as ethynylating agents with the reactions being performed in liquid ammonia or inert hydrocarbon such as hexane. Other less reactive metal ethynyls have been found to be good ethynylating agents, such as tin[90], mercury and gold (see both this and the previous chapters for Hg and Au reactions). In all these cases the starting material is a Pt(II)dihalide and the appropriate metal ethynyl.

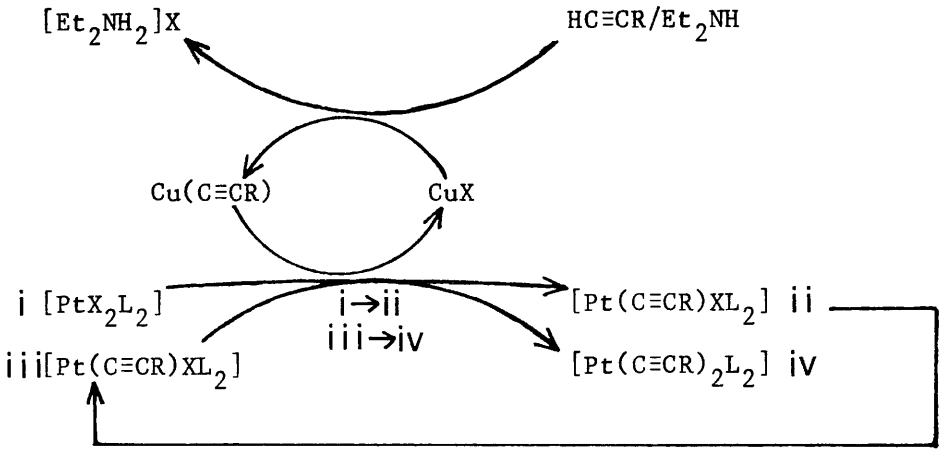
Since the terminal proton of terminal alkynes is very slightly acidic, bases will react with the ≡C-H bond. This concept has led to the utilisation of several base promoted reactions, using such bases as Ag_2O[91], NaOH[92], KOH[93], NH_3[94,92,89b] and oxalate[90d] (although in the latter case the oxalate was already bound to the platinum as $[Pt(C_2O_4)L_2]$). One very important, and probably most widely used, synthetic route has been the use of $NHEt_2$ as base and solvent, invariably with a CuI (or CuCl) catalyst added[86,95]. It is likely that copper ethynyls are the catalytic intermediates (scheme 3-1, eqn. 3.19), and indeed independant experiments show that

$$[PtX_2L_2]+2HC{\equiv}CR \xrightarrow{Et_2NH/CuI} [Pt(C{\equiv}CR)_2L_2]+2[Et_2NH_2]X \qquad (3.19)$$

copper ethynyls will act as ethynylating agents at Pt(II).[95a, 96]

Oxidative addition to Pt(0) compounds has proved successful in several cases. They fall into two classes, those where a metal ethynyl adds oxidatively to a Pt(0) centre, and those where a ligand already

Scheme 3.1 Catalytic cycle for eqn. (3.19)



Overall reaction

$$[PtX_2L_2] + 2HC{\equiv}CR \xrightarrow{CuX/Et_2NH} [Pt(C{\equiv}CR)_2L_2] + 2HX\text{-}Et_2NH \qquad (3.19)$$

bonded to Pt(0) re-arranges to give a Pt(II) ethynyl. Examples of the first class would be addition of tin ethynyls[97] or copper ethynyls[96] (eqns. 3.20, 3.21).

$$[Pt(PPh_3)_3]+Me_3Sn(C{\equiv}CMe) \longrightarrow \underline{cis}\text{-}[Pt(C{\equiv}CMe)(SnMe_3)(PPh_3)_2]+PPh_3 \qquad (3.20)$$

$$[Pt(C_2H_4)(PPh_3)_2]+2Cu(C{\equiv}CPh) \longrightarrow \underline{trans}\text{-}[Pt(C{\equiv}CPh)_2(PPh_3)_2]+2Cu \qquad (3.21)$$

Examples of ligand re-arrangement as the conversion of π-bonded acetylenes into ethynyls[98,99] (eqns. 3.22 (X=Br,I), 3.23)

$$Pt(\eta^2\text{-}XC{\equiv}CPh)(PPh_3)_2] \xrightarrow{\Delta} \underline{trans}\text{-}[Pt(C{\equiv}CPh)X(PPh_3)_2] \qquad (3.22)$$

$$[Pt\{\eta^2\text{-}(NC)C{\equiv}C(CN)\}] \xrightarrow{h\upsilon} cis\text{-}[Pt(C{\equiv}CCN)(CN)(PPh_3)_2] \qquad (3.23)$$

although eqn. 3.22 does not apply to X=Cl. PhC≡CCl will displace η^2-(PhH=CHPh) however (eqn 3.24), to give an isolable <u>cis</u> complex[98] HC≡CR(R=CF_3,C_2F_5) will also add oxidatively to $Pt(PPh_3)_4$

$$[Pt\{\eta^2\text{-}(\underline{cis}\text{-}(PhHC{=}CHPh))\}(PPh_3)_2]+HC{\equiv}CCl \longrightarrow \underline{cis}\text{-}[Pt(C{\equiv}CPh)Cl(PPh_3)_2] \qquad (3.24)$$

to produce a π-complex, but on prolonged standing in solution, and treatment with excess acetylene a bis-ethynyl complex is produced[100] (eqn. 3.25).

$$Pt(PPh_3)_4+HC{\equiv}CR \longrightarrow [Pt\{\eta^2\text{-}(HC{\equiv}CR)\}(PPh_3)_2] \xrightarrow{HC\ CR} \underline{cis}\text{-}[Pt(C{\equiv}CR)_2(PPh_3)_2] \qquad (3.25)$$

A few other methods have been discovered in specific cases <u>cis</u>-$[PtCl_2(PMe_2Ph)_2]$ will react directly with $HC{\equiv}CC(Me)_2OH$ to produce

the trans-bis(ethynyl) complex[92], whilst another direct reaction will occur between a platinum hydride and 1-ethynylcyclohexanol (eqn. 3.26) [101] accompanied by formation of the ether via dehydration from the alcohol

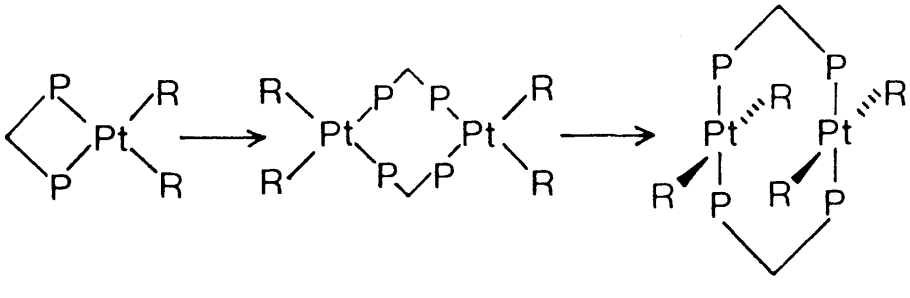
$$\text{trans-}[PtClH(PPh_3)_2] + HC\equiv C\text{-}C(OH)\text{-}\square \xrightarrow[C_6H_6]{EtOH} Cl\text{-}Pt(PPh_3)_2\text{-}C\equiv C\text{-}\square(OEt) \qquad (3.26)$$

It has been found possible to remove HCl from chlorovinyl complexes by base attack[57, 83] which produces ethynyl complexes (eqn. 3.27)

$$\text{trans-}[Pt(CCl{=}CH_2)_2(PMe_2Ph)_2] + 2Me_3N \longrightarrow \text{trans-}[Pt(PMe_2Ph)_2(C\equiv CH)_2] + 2Me_3NHCl \qquad (3.27)$$

3.4 Stereochemistry of Pt-ethynyls

Except when chelating diphosphines are employed the bis(ethynyl) products are usually trans, even from cis starting materials. With small ring chelating diphosphines, (e.g. dppm), the combination of ring opening releasing strain on the phosphine, and a favoured trans configuration usually means that further reactions will take place[102,90d] and trans bridged bimetallic species shall be formed, (eqn. 3.28), although the cis-bridged form has been detected in one case[102]



(3.28)

A few papers report cis isomers[100,96,95a,92,90] or mixtures[95b,94] Table 3.1 shows the cis-bis-ethynyl complexes so far characterised. It should be noted that even though one synthetic method may produce a

particular cis-bis(ethynyl), another may not. So for, example cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ was prepared by [94] treating $[PtCl_2(PPh_3)_2]$ with $HC{\equiv}CPh$ in aqueous ammonia, but $[Pt(C_2O_4)(PPh_3)_2]$ with $HC{\equiv}CPh$ [90d] and $[Pt(C_2H_4)(PPh_3)_2]$ with $Cu(C{\equiv}CPh)$ [96] both produced trans isomers of the product whilst in turn, both these latter methods produced cis isomers with other ethynyls (see Table 3.1). In fact, apart from the three fluoroalkynyls, all the compounds in Table (3.1) have been characterised in the trans form, it would appear then that the strongly electron withdrawing nature of the fluoroalkynyls stabilise the cis configuration. (Trans-$[Pt(C{\equiv}CCF_3)_2(PEt_3)_2]$ is known [87], but in this case the electron releasing nature of the phosphine may compensate for the electron withdrawing nature of the CF_3 group). The trans-bis-(ethynyls) show a lowering in energy of the $\pi{\rightarrow}\pi^*$ electronic transition, and it has been suggested [89f] that this indicates extended conjugation of the π-system through suitable Pt orbitals which stabilises the system.

This theory fits the observation that electron withdrawing groups will stabilise the cis configuration, as electron density will be drawn out of the π-system, weakening the extended conjugation stabilisation force and thereby making the trans isomer less stable, or conversely the cis isomer relatively more stable. With the removal of through-Pt conjugation the system would be more like other bis(organo) species (e.g. alkyls and aryls), and these are usually cis [23].

The mono(ethynyls) are all (with one exception [98]) trans, in keeping with the other known organoplatinum complexes, and without the possibility of extended conjugation, it is not surprising that all these compounds form similar geometry.

This chapter deals with some new synthetic routes to platinum

Table 3.1 Complexes cis-$[Pt(C{\equiv}CR)_2L_2]$ Previously characterised in the literature.

R	L	ref	R	L	ref
CF_3	PPh_3	[100]	Ph	PEt_3	[90d,95a]
C_2F_5	PPh_3	[100]	Ph	PBu_3	[95a]
C_6F_5	PPh_3	[96]	H	PEt_3	[95a]
Ph	PPh_3	[92,94]	H	PBu_3	[95a]
$CMe_2(OH)$	PPh_3	[92,94]	$CHCH_2$	PEt_3	[95a]
CMeEt(OH)	PPh_3	[94]	$C{\equiv}CH$	PBu_3	[95a]
CH(OH)Ph	PPh_3	[94]	$C_6H_4C{\equiv}CH$-p	PBu_3	[95a]

ethynyls, all of which produced cis-bis(ethynyls) although none did so consistently. The isomerisation of the cis→trans bis(ethynyls) is also investigated as are the implications which the factors controlling this isomerisation have on the synthesis of cis compounds.

3.5 Results and Discussion

1). Synthesis of platinum bis(ethynyl) complexes

a) Reaction in the presence of CuI catalyst

When two equivalents of HC≡CPh were added to a suspension of cis-$[PtCl_2(PMePh_2)_2]$ in diethylamine containing a trace of CuI and the whole refluxed for 10 minutes, rapid dissolution of all solid material took place. Recrystallisation of the crude product yielded white crystals whose proton n.m.r. spectrum contained a 1:4:1 triplet of triplets in the Me-P region characteristic of two phosphine ligands trans to each other. This feature is caused by "virtual coupling" of the methyl group to both phosphorous atoms giving a triplet with spacing between the two outer lines of $|^2J_{HP} + {}^4J_{HP}|$, flanked by satellites due to further coupling to ^{195}Pt ($I=\frac{1}{2}$, 34% natural abundance). Other parameters were consistent with literature values[88c] for trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (eqn. 3.29) so like the majority of

$$\text{cis-}[PtCl_2(PMePh_2)_2] + 2HC{\equiv}CPh \xrightarrow{Et_2NH/CuI} \text{trans-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] \qquad (3.29)$$

reports[86,95] it was found that this synthetic route gives trans isomers.

If the reaction was performed with just one equivalent of phenylacetylene, only a small smount (18%) of trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ was formed even after long (1hr) reflux. The main products (in nearly 1:1 ratio) were starting dihalide and trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. There was also a small amount of a tris(phosphine) species (δ 4.0(t), $^1J_{PtP}$ 3339; δ 9.6(d) $^1J_{PtP}$ 2241; $^1J_{PP}$ 20 Hz) tentatively assigned to $[Pt(C{\equiv}CPh)(PMePh_2)_3]^+$

which has probably formed from some decomposition of the products during the hour long reflux. This formation of the bis(ethynyl) shows that replacement by the second ethynyl occurs faster than dissolution and reaction of cis-$[PtCl_2(PMePh_2)_2]$ probably due to the low solubility of the dihalide complex. Furthermore no rapid disproportionation takes place between the dihalide and trans-bis(ethynyl) platinum complexes, as a mixture of the two could be kept in $CDCl_3$ solution for several days with no further reaction taking place.

When instead of adding phenylacetylene, C_2H_2 gas was passed through a diethylamine suspension of cis-$[PtCl_2(PMe_2Ph)_2]$ with some CuI catalyst present, and the reaction mixture being kept at ambient temperatures, again the (known[57]) trans complex was formed (eqn. 3.30) which was characterised from its

$$\text{cis-}[PtCl_2(PMe_2Ph)_2] + 2C_2H_2 \longrightarrow \text{trans-}[Pt(C{\equiv}CH)_2(PMe_2Ph)_2] \qquad (3.30)$$

proton n.m.r. parameters, although in this case the triplet of triplets pattern for the phosphine methyl protons was complicated by overlapping with a similar, but less intense 9 line signal from the terminal ethyne proton (see Table 3.3).

b) Reaction in the presence of NaOEt

Due to the success of HCl elimination in preparing [Au(C≡CR)L] from [AuClL] and HC≡CR in the presence of NaOEt (see previous chapter) it was thought that it might be interesting to see if platinum ethynyls could be prepared similarly. So, to a suspension of cis-$[PtCl_2(PMePh_2)_2]$ in ethanol at 0^oC, two equivalents of HC≡CPh and freshly prepared NaOEt were added. The resultant solid was filtered and recrystallisation from $CHCl_3$/pentane gave white crystals which analysed as $[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. However, the proton n.m.r. spectrum, showing only a triplet of doublets

for the phosphine methyl, ^{31}P n.m.r. parameters (δ 2.9, J_{PtP} 2298 Hz) and melting point all indicate the product is not the known trans isomer and so the product must be cis (eqn. 3.31). Furthermore the ir

$$\text{cis-}[PtCl_2(PMePh_2)_2]+2HC{\equiv}CPh+2NaOEt \longrightarrow \text{cis-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] \qquad (3.31)$$

spectrum in nujol showed two ethynyl stretching frequencies (at 2110 and 2145 cm^{-1}) again consistent with the cis isomer. However in KBr discs only one C≡C stretch was observed (at 2110cm^{-1}) so caution must be exercised in assigning product geometry from infra red data alone.

When the reaction was repeated with only one equivalent of NaOEt, then the main product was an insoluble 1:1 mixture of starting material and cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ which could be removed by filtration. This mixture could be kept in $CDCl_3$ solution for 5 days without any change, indicating that any disproportionation must be very slow. After removal of ethanol and re-dissolution of the small amount of ethanol soluble material in $CDCl_3$, ^{31}P n.m.r. spectroscopy showed that a small amount of trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ had formed, and in both this and the reaction containing two equivalents of NaOEt, the main EtOH soluble product gave a singlet in the ^{31}P n.m.r. spectrum, assigned to $MePh_2PO$, indicating that some decomposition accompanies the reaction. The formation of the cis-bis(ethynyl) shows that replacement by the second ethynyl is faster than both attack by the first ethynyl (most likely due to the greater solubility of the mono(ethynyl) over the starting dihalide complex) and also any isomerisation step which would give trans products. (The formation of trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ is probably due to a slight stoichiometric inbalance in the reagents present).

This synthetic route however is not general. With gaseous acetylenes, ethyne and propyne, reaction rates were much slower, and

in both cases, the main insoluble product was starting material. After solvent removal both samples again contained the phosphine oxide as the only ethanol soluble product (as detected by ^{31}P n.m.r. spectroscopy in $CDCl_3$).

Problems were also encountered in the reaction between phenylacetylene and cis-$[PtCl_2(PMe_2Ph)_2]$. Initial attempts at the reaction under conditions identical to those which produced cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ failed to produce any ethynyl-containing product in detectable quantities. The reaction was repeated under 4 different conditions, with 2 hour long reaction periods at 0, 20 and 60°C and 24 hrs. reaction period at 20°C. At the end of the appropriate period, the solvent was removed *in vacuo* and the phosphorus n.m.r. spectra of the resultant brown solids recorded. The product distribution is shown in Table 3.2. It can be seen that when the reaction was performed at low or room temperatures, even after 24 hrs there was less than 40% conversion to phosphine-containing products, with the major products being starting material and an unidentified species at δ-21.7 J 3510 presumably resulting from ethoxide attack at platinum. Heating to +60°C decreases the amount of both these species and the major product is now trans-mono(ethynyl) and still only very little of the bis(ethynyl) complex has formed (and at that all as the trans isomer). So clearly, the substitution in this compound is much slower than for cis-$[PtCl_2(PMePh_2)_2]$ with the formation of by-products being highly competitive.

A similar slowing of the reaction rate also occurred when the chelating diphosphine bis(di-p-tolylphosphino)ethane, (dptpe) was present. In the reaction of $[PtCl_2(dptpe)]$ with two equivalents of HC≡CPh/NaOEt after 2 hours the reaction had produced a 1:1 ratio of starting dihalide and a complex with parameters (δ 39.6 J_{PtP} 2283 Hz), typical of phosphine trans to ethynyl, assigned to $[Pt(C{\equiv}CPh)_2(dptpe)]$. A few other weak signals were present including a very weak pair of

Table 3.2 Product distribution from the reaction

cis-$[PtCl_2(PMe_2Ph)_2]$ + 2HC≡CPh/NaOEt.

δp	J_{PPt}	ASSIGNMENT	% MOLE FRACTION [a] REACTION CONDITION [b]			
			A	B	C	D
-15.3	3547	cis-$[PtCl_2(PMe_2Ph)_2]$	39.3	37.7	39.2	11.1
-7.6	2436	trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$	19.0	14.3	23.7	37.5
-12.4	2412	trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$	5.9	1.2	11.0	11.4
-21.7	3510	———	33.8	30.6	20.1	17.1
-6.2	2806	———	5.6	4.0	7.7	0.9
34.0	0	$OPMe_2Ph$	13.8	16.5	12.3	8.4

a cis % of the total product (by integration of spectra)

b Reaction conditions: A Time 2 hrs. Temp. 0°C

B " 2 hrs. " 20°C

C " 24 hrs " 20°C

D " 2 hrs " 60°C

doublets (δ 41.8, 36.3. $^{2}J_{pp}$ 5.3Hz) which by independent experiment due to/P (see 3-5.1.e later) were shown to be due to cis-[Pt(C≡CPh)Cl(dptpe)]. After 30 minutes reflux with excess HC≡CPh/NaOEt, the reaction proceeded further, consuming all the starting material and giving mainly [Pt(C≡CPh)$_2$(dptpe)] (50%) plus several decomposition products. Interestingly a similar reaction between [PtCl$_2$(dptpe)] and ethyne in the presence of EtONa produced none of the expected ethynyl- containing products, only starting material and the same set of signals for decomposition products in approximately the same ratio, indicating that these signals are not due to alkynyl — containing material.

The failure of these reactions may indicate that whereas formation of ethynyls probably occurs via ethynyl anion formation (as appears to be the case for the analogous preparation of gold ethynyls), with less electron withdrawing groups in the alkyne and with certain phosphines on platinum, other reaction pathways become possible, either by ethoxide attack at the metal centre or else by base induced decomposition of the initial reaction products. Whatever the reaction it is clear that this synthetic route is less versatile for platinum ethynyls than gold ethynyls.

(c) via Pt carbonyl complexes

A second partially successful synthetic route to cis-bis(ethynyl) complexes was found using platinum carbonyl complexes as intermediates. Complexes of the type cis-[Pt(C≡CR)$_2$(CO)(PMePh$_2$)], though unstable in solution at room temperature can be easily prepared from cis-[PtCl$_2$(CO)-(PMePh$_2$)], Hg(C≡CR)$_2$ and Et$_4$Cl [54]. The same bis(ethynyl) carbonyl complexes could also be prepared using phosphinegold(I)ethynyls (eqn 3.32).

$$\underline{cis}\text{-}[PtCl_2(CO)(PMePh_2)]+2[Au(C{\equiv}CPh)(PPh_3)] \longrightarrow \underline{cis}\text{-}[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]+2[AuCl(PPh_3)]$$

The mercury route had the advantage that the by-product was the $CHCl_3$-insoluble salt $[Et_4N]_2[Hg_2Cl_6]$ which could be removed by filtration although care was needed as this by-product could also catalyse the cis→trans isomerisation of the desired products (see below).

When one equivalent of $PMePh_2$ was added to a freshly prepared solution of cis-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$ rapid displacement of the carbonyl took place giving cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (eqn 3.33) in near quantitative yield.

$$\underline{cis}\text{-}[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]+PMePh_2 \longrightarrow \underline{cis}\text{-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2]+CO \qquad (3.33)$$

Similarly PPh_3 displaced CO from cis-$[Pt(C{\equiv}CPh)_2(CO)(PPh_3)]$ producing cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$.

When one equivalent of PPh_3 was added to a solution of cis-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$ again a very rapid reaction occurred. After 15 minutes the ^{31}P nmr spectrum showed signals for cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ and cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ as well as a pair of doublets (δ16.8 $^1J_{PtP}$ 2333, δ-3.2 $^1J_{PtP}$ 2252, $^2J_{PP}$ 20.7Hz) assigned to the expected product cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)(PPh_3)]$, with a statistical distribution of the products (i.e. 2 equivalents of the mixed phosphine complex per equivalent of the symmetrical phosphine compounds, which were present in equal amount), so the phosphine exchange that occurred to produce the symmetrical products must have been as fast as the carbonyl displacement. Furthermore, since all the products

were cis in the above reactions, free CO cannot catalyse a rapid cis→trans isomerisation of the products.

The propynyl complex cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ is more difficult to isolate, being much more prone to decomposition, however it can be prepared and subsequently stored at -60^oC for short periods. When one equivalent of $PMePh_2$ was added to a solution of the bis(propynyl) complex, a white crystalline material was isolated. Analysis showed this to be $[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$ but the PtP coupling constant of 2588 Hz and the distinctive triplet of triplets for the phosphine methyl groups (see Table 3.3) showed that only the trans isomer was isolated. The reaction was repeated and carefully followed by ^{31}P nmr spectroscopy. To pure cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ (δ-3.0 PtP 2094Hz), 0.33 mole equivalent of $PMePh_2$ was added. As expected 66% of the product was starting material with other signals at δ1.2 J 2578 and δ5.2 J 2573 assigned to trans-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$ and trans-$[Pt(C{\equiv}CMe)Cl(PMePh_2)_2]$ respectively (the latter by analogy to the phenylethynyl reactions; it was also seen as an intermediate in reactions between $Hg(C{\equiv}CMe)_2$, and cis-$[PtCl_2(PMePh_2)_2]$ (see section 3.5.1.e)). Doubling the amount of phosphine produced an increase in the strength of these signals, plus rapid growth of a new signal at δ-2.1 $^1J_{PtP}$ 2315, assigned from the coupling constant to cis-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$, accounting for 32% of the species in solution. When the amount of phosphine was increased to 1.0 equivalent, no starting carbonyl remained and the ratio of cis : trans-bis(ethynyl) was 1:2. After 10 minutes standing at room temperature however only a trace of the cis complex remained and after a further 10 minutes only trans-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$ (with $\sim$ 20% of the trans-mono ethynyl) remained. This rapid isomerisation prevented the isolation of the cis-bis(ethynyl), and it should be noted that no propynyl complexes have been isolated in the

Table 3.3 Nmr parameters for $[Pt(C{\equiv}CR)_2L_2]$

R	L_2	isomer	^{31}P		^{1}H		
			δ	J	δ[a]	J_{PH}[b]	$^3J_{PtH}$
Ph	$(PPh_3)_2$	cis	16.7	2328			
		trans	18.6	2649			
	$(PMePh_2)_2$	cis	-2.0	2298	1.91	9.0	27.3
		trans	1.4	2536	2.42	7.4	33.3
	$(PMe_2Ph)_2$	cis	-17.8	2254	1.70	9.3	32.3
		trans	-12.4	2418	2.08	7.3	32.3
	$(PMe_2Ph)(PPh_3)$	cis	16.8[e] -3.2	2333 2252			
	(dptpe)	cis	39.6	2288			
Me	$(PMePh_2)$	cis	-2.1	2315			
		trans	1.2	2588	2.28[c]	7.3	33.0
H	$(PMe_2Ph)_2$	trans			2.03[d]	7.5	32.2

a For MeP groups.

b $^2J_{PH}$ for cis isomers $|^2J_{PH}+{}^4J_{PH}|$ for trans.

c $C{\equiv}C\underline{C}H_3$ δ1.49, J_{PtH} 14.7Hz

d $C{\equiv}C\underline{H}$ δ2.14, $^4J_{PH}$ 2.3, $^3J_{PtH}$ 44Hz

e $^2J_{PP}$ 21Hz

cis form, propynyl ligands appearing to have a greater propensity for the trans geometry.

Attempts to prepare cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ by this route also failed and the known[57] trans isomer was isolated (see Table 3.3 for parameters). In this case after Et_4NCl had been added to the mixture of cis-$[PtCl_2(CO)(PMe_2Ph)]$ and $Hg(C{\equiv}CPh)_2$, the solution was stirred for 5 minutes and then filtered. Phosphine was added immediately but more $[Et_4N]_2[Hg_2Cl_6]$ precipitated out at this stage indicating that it had not been completely removed by the initial filtration. It is known that mercury salts catalyse the cis→trans isomerisation (see section 3.5.2.) and this could explain why only trans isomers are formed in this case.

Using half the amount of mercury salts the mono(ethynyl) carbonyl complexes can be prepared[54]. These, like the bis(ethynyl)carbonyl intermediates, have the phosphine and carbonyl in a mutually cis arrangement (with the most stable isomer having the ethynyl trans to carbonyl). Addition of phosphine to these complexes produced only the trans-mono(ethynyl)product (eqn. 3.34 R=Me,Ph) due to the rapid cis→trans isomerisation of $[Pt(C{\equiv}CR)Cl(PMePh_2)_2]$

$$\text{cis-}[PtCl_2(CO)(PMePh_2)]+\tfrac{1}{2}Hg(C{\equiv}CR)_2+\tfrac{1}{2}Et_4NCl \longrightarrow \underset{\text{trans-}[Pt(C{\equiv}CR)Cl(PMePh_2)_2]}{[Pt(C{\equiv}CR)Cl(CO)(PMePh_2)]} \xrightarrow{PMePh_2} \quad (3.34)$$

A third possible method looked likely using the intermediate $[Pt(C{\equiv}CR)_2(cod)]$ (cod = 1,5-cyclooctadiene) which is a complex with the ethynyl groups necessarily in the cis position. Phosphine replacement of the di-olefin ligand would be expected to give $[Pt(C{\equiv}CR)_2L_2]$ and there would be a good chance that the product would be cis, the intermediate would be $[Pt(C{\equiv}CR)_2(cod)(L)]$ with the cod acting as a monodentate ligand.

Given that olefins and carbonyls have very similar bonding and reactivity towards platinum (see Chapter 5), this complex then resembles $[Pt(C{\equiv}CR)_2(CO)L]$, the intermediate shown in section 3.5.1.c., which is only found in the cis form. So even if the phosphine replacement of the monodentate cod was slow the products still have a good chance of retaining their cis geometry. Such phosphine replacement of cyclooctadiene has been used before [103] in the preparation of $[PtR_2L_2]$ and $[PtRClL_2]$ (L = PPh_3, dppe, R = aryl) (eqn 3.35), although in this case the cis-bis(aryl) was formed. For these complexes this is the more stable isomer

$$[PtCl_2(cod)] + 2SnMe_3R \longrightarrow [PtR_2(cod)] \xrightarrow{2L} \underline{cis}[PtR_2L_2] \qquad (3.35)$$

(i) Preparation of $[Pt(C{\equiv}CPh)_2(cod)]$

When a solution of phenylacetylene and sodium ethoxide was added to a suspension of $[PtCl_2(cod)]$ in ethanol there was a slight colour change although the solid still remained. Filtration of this solid yielded $[Pt(C{\equiv}CPh)_2(cod)]$ (eqn. 3.36), a bis(phenylethynyl) complex, which by the nature of the other ligand must almost certainly be in the cis configuration. The complex proved difficult to recrystallise, decomposing in hot $CHCl_3$ but finally successive

$$PtCl_2(cod) + 2HC{\equiv}CPh + 2NaOEt \longrightarrow [Pt(C{\equiv}CPh)_2(cod) + 2NaCl + 2EtOH \qquad (3.36)$$

re-crystallisations at lower temperatures from CH_2Cl_2 produced white crystals of the pure product. (In the subsequent reactions of this complex, the initial EtOH insoluble crude product was used). The

compound could also be prepared from the reaction between cis-$[PtCl_2(cod)]$ and $[Hg(C{\equiv}CPh)_2]$ but decomposition accompanied the reaction and yields were low with the product being impure. Neither method could be used to prepare $[Pt(C{\equiv}CMe)_2(cod)]$ due to decomposition reactions and like the carbonyl complexes with propynyl ligands, the compound is more prone to decomposition than the phenylethynyl analogue.

(ii) Reactions of $[Pt(C{\equiv}CPh)_2(cod)]$ with phosphines.

Treatment of $[Pt(C{\equiv}CPh)_2(cod)]$ in CH_2Cl_2 under N_2 atmosphere with either $PMePh_2$ or PPh_3 led to the rapid formation of the cis-bis(phosphine) complexes (eqn. 3.37, L = $PMePh_2$, PPh_3). Usually a trace of trans-mono(ethynyl)chloride complex was

$$[Pt(C{\equiv}CPh)_2(cod)]+2L \longrightarrow \text{cis-}[Pt(C{\equiv}CPh)_2L_2]+cod \qquad (3.37)$$

detectable. The source of chloride is probably the chloride impurities in the crude starting $[Pt(C{\equiv}CPh)_2(cod)]$, most likely partially ethynylated species. With PMe_2Ph, the proton nmr of the crude product (formed by solvent removal in vacuo after phosphine addition to the $[Pt(C{\equiv}CPh)_2(cod)]$) contained a triplet of doublets with parameters consistent for cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ (see Table 3.2). However on recrystallisation isomerisation occurred producing a white product with proton and phosphorous nmr parameters consistent with trans-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$. (The assignment of the crude product to cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ was confirmed when a separate experiment (see section 3.5.1.f.) a complex with identical parameters was observed and seen to isomerise to the trans form). Although no species known to

catalyse the isomerisation is present trans products are still obtained and it should be noted that no cis products have ever been isolated with PMe_2Ph. The reason for this may well be a mixture of steric and electronic effects. Sterically PMe_2Ph is less bulky than any of the phosphine ligands which give cis isomers, the Tolman cone angles being PMe_2Ph (122^o) PBu_3 = PEt_3(132^o) $PMePh_2$ (136^o) PPh_3(145^o)[104] However, as the cone angle increases so the s-character in the phosphine lone pair decreases, so that the bulky ligands are poorer s-electron donors to Pt. As mentioned earlier (section 3.4) electron withdrawing groups on the alkynyl appear to increase the relative stability of the cis isomer over trans, and it seems likely that bulky phosphines, by lowering the s-electron density at Pt also stabilise the cis isomer for the same reason, although clearly there is a great dependence on the synthetic route chosen in deciding which isomer is formed.

(e) Reactions from $[PtCl_2L_2]$ and $[Hg(C{\equiv}CR)_2]$

Following the success in using mercury complexes as organogroup transfer agents in the reactions with $[PtCl_2(CO)L]$ (see section 3.5.1c) the reactions of $Hg(C{\equiv}CR)_2$ (R=Me,Ph) with cis-$[PtCl_2L_2]$ were investigated.

When a chloroform solution of cis-$[PtCl_2(PMePh_2)_2]$ was treated with $Hg(C{\equiv}CPh)_2$ (2 molar equivalents) a grey precipitate developed due to insoluble mercury by-products. After filtration, the solvent was evaporated, and ^{31}P nmr spectroscopy of the product showed that the main product was trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ with some trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ by-product but no trace of the cis isomers (eqn. 3.38).

$$cis\text{-}[PtCl_2(PMePh_2)_2] + 2Hg(C{\equiv}CPh)_2 \longrightarrow trans\text{-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] + 2[Hg(C{\equiv}CPh)Cl] \quad (3.38)$$

Use of Et_4NCl as symmetrising agent to transfer both ethynyls from mercury to platinum did not change the reaction product geometry (although when followed carefully by ^{31}P nmr spectroscopy some reactions produced up to 50% of the cis-bis(ethynyl) but its isomerisation to the trans form, catalysed by Hg salts prevented its isolation) The formation of some cis isomer is indicative of a faster reaction rate of the mercury compounds when Cl^- is present due to the rapid formation of the insoluble $[Et_4N]_2[Hg_2Cl_6]$.

When half the amount of $[Hg(C{\equiv}CPh)_2]$ was used the mono-(ethynyl) platinum complex was formed and this forms an interesting comparison with the base promoted methods where bis(ethynyls) are produced (eqn. 3.39). Treatment of a pure sample of this product with further $[Hg(C{\equiv}CPh)_2]$ produced the trans-bis(ethynyl) so in the formation of the

$$\text{cis-}[PtCl_2(PMePh_2)_2]+Hg(C{\equiv}CPh)_2 \longrightarrow \text{trans-}[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]+[Hg(C{\equiv}CPh)Cl]$$

latter complex by eqn.(3.38) trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ is a likely intermediate. When preparation of the mono(ethynyl) platinum complex was attempted using Et_4NCl symmetrising agent, after rapid filtration of the initial insoluble product, cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ was detectable by ^{31}P nmr spectroscopy along with starting dihalide, trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ and a pair of doublets. (δ 3.6, $^1J_{PPt}$ 2325 ; δ-4.8, $^1J_{PPt}$ 3672; $^2J_{PP}$ 18Hz). The PPt coupling constants for the last complex are typical for phosphines trans to ethynyl and chloride respectively, whilst the PP coupling constant implies a cis-bis(phosphine) arrangement. These signals are therefore assigned to cis-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$. Reaction continued with unreacted mercury complex until after 20 minutes only

trans-[Pt(C≡CPh)Cl(PMePh$_2$)$_2$] and unreacted starting dichloride remained. (The reaction could not have continued via ligand exchange reactions amongst the platinum complexes as cis-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] has been prepared in the presence of cis-[PtCl$_2$(PMePh$_2$)$_2$] and trans-[Pt(C≡CPh)Cl-(PMePh$_2$)$_2$] (see section 3.5.1b) without undergoing further reactions). The reaction mechanism is shown in scheme 3.2 which shows the reactions of cis-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$] with mercury salts, a key step in the cis → trans isomerisation of these complexes, and will be discussed more fully in section 3.5.2. The formation of any bis(ethynyls), and particularly the cis isomer again points to the increase in rate of ligand exchange when Cl^- is present.

With mercury propynyls similar results were obtained with trans-[Pt(C≡CMe)$_2$(PMePh$_2$)$_2$] or trans-[Pt(C≡CMe)Cl(PMePh$_2$)$_2$] being the main products depending on the ratio of [Hg(C≡CMe)$_2$] to cis-[PtCl$_2$(PMePh$_2$)] used. The products were identified by ^{31}P nmr spectroscopy. Trans-[Pt(C≡CMe)Cl(PMePh$_2$)$_2$] was not isolated, but its identity deduced by comparison of its preparation, spectroscopic parameters (see Table 3.4) and reactions with the known trans-[Pt(C≡CPh)Cl(PMePh$_2$)$_2$]. (It was also detected in the reaction of cis-[Pt(C≡CMe)$_2$(CO)(PMePh$_2$)] with PMePh$_2$ - see section 3.5.1c.). Cis-intermediates were never detected, reflecting a faster isomerisation of cis propynyl complexes compared with their phenylethynyl analogues.

Starting from bis(dimethylphenylphosphine)platinum dichloride, cis-[PtCl$_2$(PMe$_2$Ph)$_2$], under conditions identical to those which produced trans-[Pt(C≡CPh)$_2$(PMePh$_2$)$_2$], [Hg(C≡CR)$_2$] (R=Ph,Me) produced only the trans-mono(ethynyl) products and in poor (<50%) yield, with starting material being the only other product. This resembles the reactions of NaOEt/HC≡CPh with cis-[PtCl$_2$(PMe$_2$Ph)$_2$] (see section 3.5.1c) which were

Scheme 3.2 Reaction of $[PtCl_2(PMePh_2)_2]$ with $Hg(C{\equiv}CPh)_2$

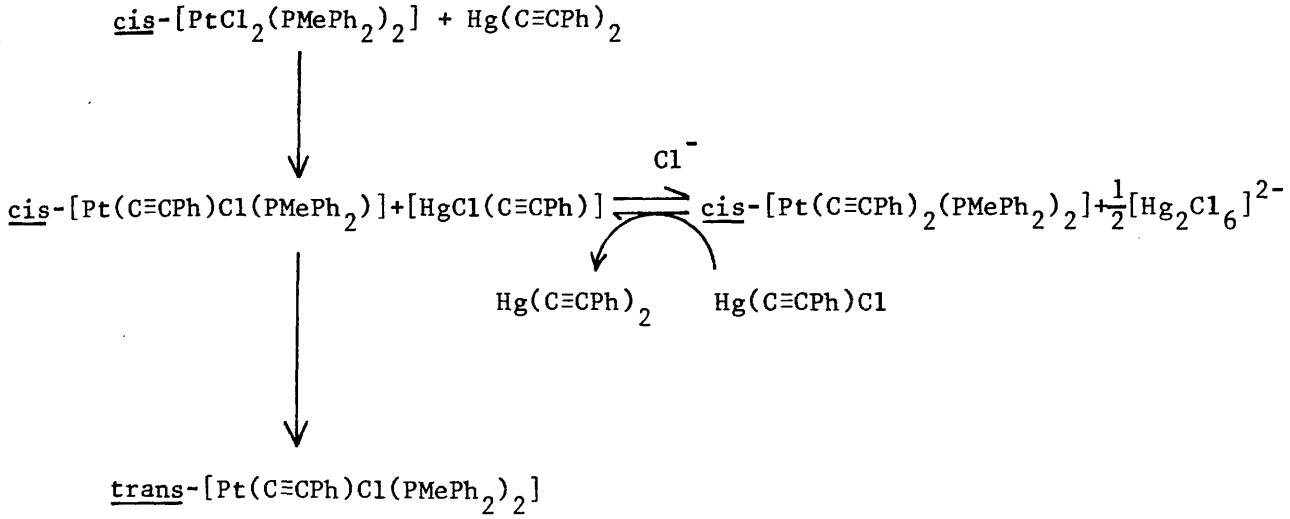


Table 3.4 Nmr parameters for mono-ethynyl complexes $[Pt(C{\equiv}CR)XL_2]$

R	L_2	X	^{31}P			
			cis		trans	
			δ	J_{PPt}	δ	J_{PPt}
Ph	$(PPh_3)_2$	Cl	14.9	4441	21.5	2661
			18.6	1755		
		Br	16.1	1782	20.7	2623
			15.3	4423		
		I			18.2	2556
	$(PMePh_2)_2$	Cl	-4.8	3672	5.1[a]	2547
			3.6	2325		
		Br			3.2	2606
		I			5.2	2539
	$(PMe_2Ph)_2$	Cl			-7.5[c]	2439
	(dptpe)	Cl	41.9	2334		
			36.4	3638		
Me	$(PMePh_2)_2$	Cl			5.0[b]	2580
	$(PMe_2Ph)_2$	Cl			-7.5	2436

a δMeP 2.22, $|^2J_{PH}+^4J_{PH}|$ 7.4Hz, $^3J_{PtH}$ 30.3Hz

b δMeP 2.22, $|^2J_{PH}+^4J_{PH}|$ 7.7Hz, $^3J_{PtH}$ 30.0Hz, δ C≡CMe unresoluable

c δMeP 1.88 $|^2J_{HP}+^4J_{HP}|$ 7.5Hz, $^3J_{PtH}$ 30.0Hz

found to proceed more slowly than the analogous reactions of cis-$[PtCl_2(PMePh_2)_2]$ and which failed to produce bis(ethynyl) complexes in significant amounts. This must be due to a combination of steric and electronic factors hindering nucleophilic attack at platinum (or conversely electrophilic attack by platinum at mercury).

Trans products were also observed when $[Hg(C{\equiv}CPh)_2]$ transferred ethynyl groups to cis-$[PtCl_2(PPh_3)_2]$. Again cis-intermediates could be detected when Et_4NCl was present, although this time only the cis-mono (ethynyl) was observed (see Table 3.4). (The same pair of doublets was generated when cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ was treated with $HgCl_2$ (see section 3.5.2), thus confirming its assignment). The complex cis-$[Pt(C{\equiv}CPh)ClL_2]$ possesses a much greater stability when $L=PPh_3$ compared to $L=PMePh_2$. For instance when $L=PPh_3$ the complex takes over 24 hours to completely isomerise to the trans form, compared with a few minutes when $L = PMePh_2$. The isomerisation rate of the former was unaffected by heating to $+60^{o}C$ or addition of free PPh_3. It could therefore be prepared in much higher concentrations and it is not surprising that the only cis-mono(ethynyl) isolated and characterised (even including chelating diphosphines) is cis-$[Pt(C{\equiv}CPh)Cl(PPh_3)_2]$ [98].

The reactions of $[PtCl_2(dptpe)]$ with $Hg(C{\equiv}CPh)_2$ produced complexes which by the nature of the phosphine must be cis. So reaction of the two complexes with or without Et_4NCl present produced a species with parameters δ39.6 J_{PtP} 2335, which was assigned to $[Pt(C{\equiv}CPh)_2(dptpe)]$ (cf section 3.5.1b). These parameters differ from those for this complex prepared via $[PtCl_2(dptpe)]$ and HC≡CPh/NaOEt ($^1J_{PtP}$ 2283) due to the interaction of the mercury salts (see 3.5.4). Also detectable were a pair of doublets (δ41.9, $^1J_{PtP}$ 2334 ; δ36.4, $^1J_{PtP}$ 3638 ; $^2J_{PP}$ 6.2 Hz) assigned to cis-$[PtCl(C{\equiv}CPh)(dptpe)]$, although it was only present in a small (∿20%) amount.

f) Reactions from $[PtCl_2L_2]$ and $[Au(C{\equiv}CR)L']$

The previous chapter showed a great similarity of gold and mercury ethynyls in their reactions towards cis-$[PtCl_2(CO)(PMePh_2)]$. Similarly their reactions with cis-$[PtCl_2(PMePh_2)_2]$ closely resembles each other. So when cis-$[PtCl_2(PMePh_2)_2]$ is allowed to react with two molar equivalents of $[Au(C{\equiv}CPh)(PPh_3)]$, the final product is trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (eqn. 3.40). However when followed by ^{31}P nmr spectroscopy,

$$\text{cis-}[PtCl_2(PMePh_2)_2]+2[Au(C{\equiv}CPh)(PPh_3)]\rightarrow\text{trans-}[Pt(C{\equiv}CPh)_2(PMePh_2)_2] + 2[AuCl(PPh_3)] \qquad (3.40)$$

again a more complicated reaction was observed. In one case (out of a total of five runs of the experiment), the major product was the cis-bis-(ethynyl), and the spectrum showed two sharp peaks in the region of the spectrum containing signals for the gold complexes throughout the reaction, which was rapid and complete in 30 minutes. In all other cases the trans-mono(ethynyl) complex was the major initial product followed by a slow (2 day) conversion to the trans-bis(ethynyl). When this pathway was followed the spectra contained one broad signal for the gold complexes, and broadened signals for the platinum compounds. The fast exchange could be stopped by cooling to $-60^{o}C$, and was shown to be due to free phosphine when addition of sulphur at room temperature caused a sharpening of all the signals, including separating the gold signals into its separate components of $[AuCl(PPh_3)]$ and $[Au(C{\equiv}CPh)(PPh_3)]$. Furthermore if sulphur was added immediately after mixing the platinum and gold starting materials, the main product was again cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. Free phosphine which is likely to have arisen from a trace of decomposition (or impurity in) one of the species present, does not catalyse the cis → trans isomerisation of the product (see section 3.5.2) and the effect it has seems to be that

of causing [Au(C≡CPh)(PPh_3)] to undergo exchange with [AuCl(PPh_3)] (as observed before see Chapter 2). It thereby provides a second reaction pathway for the gold ethynyl and lowers its reactivity towards platinum, thus slowing the second ethynyl transfer down sufficiently to allow isomerisation of the mono(ethynyl) intermediate, which is known to be a rapid spontaneous reaction (see previous section). If traces of free phosphine are not present, either by chance or by addition of S_8 scavenger, the second transfer proceeds at a rate faster than the isomerisation step and the cis-bis(ethynyl) can be isolated. So possibly the Au ethynyls prove better than Hg ethynyls for producing cis platinum bis-ethynyls if S_8 is present.

If cis-[$PtCl_2(PMe_2Ph)_2$] was allowed to react similarly with [Au(C≡CPh)(PPh_3)] in $CDCl_3$ after 90 minutes the main product (60%) was a species with parameters δ_P -17.8, J_{PtP} 2254 and a methylphosphine signal in the proton nmr consisting of a triplet of doublets (δ_{MeP} 1.70 $^2J_{PH}$ 9.3, $^3J_{PtH}$ 27.3) which was assigned to cis-[$Pt(C{\equiv}CPh)_2(PMe_2Ph)_2$] which was present along with trans-[$Pt(C{\equiv}CPh)_2(PMe_2Ph)_2$] (30%) and trans-[Pt(C≡CPh)-Cl($PMe_2Ph)_2$] (10%). Like those cases in the similar reactions with cis-[$PtCl_2(PMePh_2)_2$] which produced cis-bis(ethynyl) products (see previous paragraph) the gold phosphine signals were sharp and distinct for the two components. On standing at room temperature for 4 days, the cis material isomerised to trans-[$Pt(C{\equiv}CPh)_2(PMe_2Ph)_2$], an isomerisation which prevented the cis compound's isolation. Like the reactions of PMe_2Ph with [$Pt(C{\equiv}CPh)_2$(cod)] where this cis product was formed and underwent isomerisation to the trans form (see section 3.5.1d) no recognised catalyst for the isomerisation was present, and so the dimethylphenyl complexes in this case seem to be maintaining their propensity for trans products, although as explained previously (section 3.5.1d) the reasons for this are not understood.

CONCLUSIONS

The cis → trans isomerisation step has been shown to take place at the mono(ethynyl) intermediate (see 3.5.2). If the reaction conditions are such that the replacement of the second ethynyl is faster than the competing isomerisation then cis products will be produced, if not then trans products will dominate. This is illustrated by reactions involving NaOEt or CuI where for the latter formation and exchange may be significantly slower than the reaction involving the strong base. Mercury and copper halides are now known to catalyse the cis → trans isomerisations of $[Pt(C{\equiv}CR)_2L_2]$ (see section 3.5.2) but the reactions are unlikely to be fast enough to account for the formation of trans isomers in the synthetic preparations. (This is certainly true for mercury halides where the preparations and isomerisation studies were both performed in chloroform, for copper halides it is less certain as the solvent used for isomerisation reactions ($CDCl_3$) differs from that of the preparations (Et_2NH)). This does not apply to the reactions from cis-$[Pt(C{\equiv}CR)_2(CO)L]$ and $[Pt(C{\equiv}CPh)_2(cod)]$ where the ethynyls are already present, and here the failure to obtain cis-bis(ethynyls) from L = PMe_2Ph or R = Me must be due to a generally lower kinetic stability of the cis complexes making isomerisation to the trans form more favourable. Other workers [95b] have also reported a dependance of phosphine and ethynyl substituents on product geometry although the reasons for these changes are not well understood at present. The effect of electron density at Pt with changing the phosphine cone angle may play a part.

3.5.2 Isomerisation of cis-bis(ethynyl)platinum complexes

As mentioned in the introduction, for complexes of the type $[Pt(C{\equiv}CR)_2L_2]$ the trans form is thermodynamically favoured. Nevertheless

solutions of cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ in $CDCl_3$ are unaffected by reflux or prolonged standing at room temperature. Furthermore, addition of 0.1 molar equivalent of free phosphine or iodide (as the soluble complex $[Bu_4N]I$) both have no effect on the geometry of the complex (Anderson [19d] also reported failure to convert cis-$[Pt(C{\equiv}CPh)_2(PEt_3)_2]$ to its trans form by addition of free PEt_3). Both these reagents are well known as catalysts for nucleophilic catalysed isomerisations of square planar complexes [23] such as $[PtCl_2(PEt_3)]$ [105] and $[PtCl_2(CO)(PMe_2Ph)]$ [106] and it is clear that cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ possesses a high kinetic stability.

Addition of small amounts of mercury halides, however, bring about immediate isomerisation of the cis form. When followed by ^{31}P nmr spectroscopy addition of about 10% of HgX_2 (X = Cl, Br, or I) to a $CDCl_3$ solution of cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ caused complete conversion to the trans form in 3 hours at ambient temperature. For X = Cl the growth of signals due to a very small amount of cis-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$, followed by trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ before any trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ was apparent. At the end of the reaction trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ in an amount equivalent to the amount of $HgCl_2$ added remained. With X = Br and I it was not possible to detect any of the cis-mono(ethynyl) intermediates, probably due to a greater rate of isomerisation with these halides (the rate of isomerisation of $[PtX_2(CO)(PMePh)]$ and $[PtX_2(C_2H_4)(PMe_2Ph)]$ was also found to increase in the order Cl<Br<I (see chapter 5)). Also, due to the increased reaction rate, it proved impossible to detect any trans-mono(ethynyl) before the appearance of the trans-bis(ethynyl).

The isomerisation proceeded just as quickly when $[Hg(C{\equiv}CPh)Cl]$ (0.1 molar equivalent) was used as the catalyst. (The catalyst was prepared from a 1:1 reaction of $HgCl_2$ and $Hg(C{\equiv}CPh)_2$ in EtOH and added by syringe immediately after being prepared. EtOH itself cannot cause isomerisation

as the cis isomer could be prepared in this solvent). In this case trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ was still present at the end of the reaction, as $Hg(C{\equiv}CPh)Cl$ disproportionates to $Hg(C{\equiv}CPh)_2$ and $HgCl_2$ and the latter would react with trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ to give the mono(ethynyl).

An analogous reaction pathway was found in the isomerisation of cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ with HgX_2 (X=Cl,Br,I) but as mentioned previously the isomerisation of the cis-mono(ethynyl) halide is much slower with this phosphine. Five minutes after addition of one equivalent of $HgCl_2$ to cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$, apart from 20% of starting materials the only product was cis-$[Pt(C{\equiv}CPh)Cl(PPh_3)_2]$ identified by its ^{31}P nmr parameters (see Table 3.4). Fifteen minutes later no starting bis(ethynyl) remained and trans-$[Pt(C{\equiv}CPh)Cl(PPh_3)_2]$ had grown in to account for 13% of the product. This steadily grew in over a period of 24 hrs as the cis-mono ethynyl underwent isomerisation, although in this period cis-$[PtCl_2(PPh_3)_2]$ also grew in accompanied with the precipitation of unidentified compounds arising probably from decomposition or disproportionation of the cis-mono (ethynyl). Addition of 0.05 molar equivalent of Ph_3P did not increase the rate of isomerisation, so this is not a reaction subject to nucleophilic catalysis. With smaller amounts of $HgCl_2$ (0.2 molar equivalent), the pair of doublets for the cis-mono(ethynyl) complex is much weaker (due to the smaller amount of halide present to react with the starting material) and trans-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ was observed to grow in after the appearance of trans-$[Pt(C{\equiv}CPh)Cl(PPh_3)_2]$, the former growing steadily in over a period of 24 hrs. In this case, complete isomerisation was never achieved and with prolonged standing (4 days) again cis-$[PtCl_2(PPh_3)_2]$ was formed and a precipitate had formed in the nmr tube.

The overall isomerisation sequence is represented by equations (3.41) to (3.44) (X=Cl, Br, I : L = $PMePh_2$, PPh_3) with the catalytic cycle

being the sequence of equations (3.42) to (3.44) (as shown diagramatically in scheme 3.3). The mercury bis(ethynyl) must be formed as [Hg(C≡CPh)X]

$$\underline{cis}\text{-}[Pt(C{\equiv}CPh)_2L_2]+HgX_2 \longrightarrow \underline{cis}\text{-}[Pt(C{\equiv}CPh)XL_2]+Hg(C{\equiv}CPh)X \qquad (3.41)$$

$$\underline{cis}\text{-}[Pt(C{\equiv}CPh)_2L_2]+Hg(C{\equiv}CPh)X \rightarrow \underline{cis}\text{-}[Pt(C{\equiv}CPh)XL_2]+Hg(C{\equiv}CPh)_2 \qquad (3.42)$$

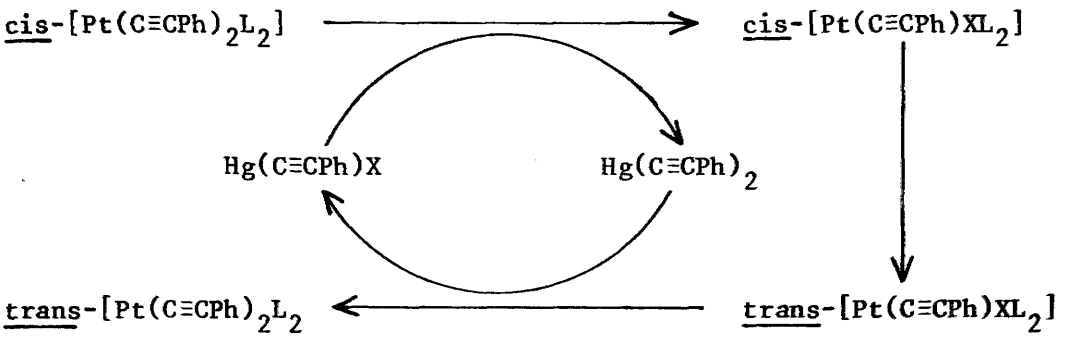
$$\underline{cis}\text{-}[Pt(C{\equiv}CPh)XL_2] \longrightarrow \underline{trans}\text{-}[Pt(C{\equiv}CPh)XL_2] \qquad (3.43)$$

$$\underline{trans}\text{-}[Pt(C{\equiv}CPh)XL_2]+Hg(C{\equiv}CPh)_2 \longrightarrow \underline{trans}\text{-}[Pt(C{\equiv}CPh)_2L_2]+Hg(C{\equiv}CPh)X \qquad (3.44)$$

will not transfer its second phenylethynyl group as seen in the preparative reaction of the trans-mono(ethynyl) complexes (eqn 3.38). Also platinum complexes do not act as catalytic intermediates as cis-$[Pt(C{\equiv}CPh)_2L_2]$ does not react with trans-$[Pt(C{\equiv}CPh)_2L_2]$ and/or trans-$[Pt(C{\equiv}CPh)XL_2]$ as checked by independently adding some of these compounds to samples of pure cis-bis(ethynyl). This rules out the possibility of the isomerisations proceeding via Pt-ethynyl/halide exchange. Isomerisation of $[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ proceeds equally fast in $CDCl_3$ or toluene but is much more rapid in tetrahydrofuran where isomerisation is accompanied by precipitation of the non-polar trans product. The increase in rate could be due to either the fact that $HgCl_2$ is more soluble in this solvent or else a difference in the cis → trans isomerisation of the mono(ethynyl). (Kemmitt, when he prepared cis-$[Pt(C{\equiv}CPh)Cl(PPh_3)_2]$ reported[98] a solvent dependency on this isomerisation.)

This isomerisation mechanism, involving reversible exchange of ligands between metals, is very unusual for platinum complexes and none have been described previously in the literature, with other pathways[23] described involving 5 co-ordinate associative or 3 co-ordinate dissociative

Scheme 3.3 Catalytic cycle for the cis→trans isomerisation of $[Pt(C{\equiv}CPh)_2L_2]$



intermediates, or else following photochemical or oxidative addition/reductive elimination routes.

Other mercury complexes will also catalyse this isomerisation. $[Et_4N]_2(Hg_2Cl_6]$ (prepared from $HgCl_2$ and Et_4NCl in ethanol) was just as effective as $HgCl_2$ in isomerising cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ with the reaction being complete in 2½ hours (in $CDCl_3$) and again a small amount of the trans-mono(ethynyl) complex remaining. It is not known whether $[Hg_2Cl_6]^{2-}$ is acting as the catalyst or whether dissociation of the anion back to $HgCl_2$ and Cl^- is taking place, although the formation of the mono(ethynyl) suggests the latter is the case. PhHgCl also catalysed the cis → trans isomerisation, although much more slowly, with only about 20% of trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ being formed after 24 hours showing that $[HgPh(C{\equiv}CPh)]$ is a much less useful ethynylating agent than $[Hg(C{\equiv}CPh)_2]$.

Copper(I) iodide also catalyses the cis → trans isomerisation although it acts much more slowly than $HgCl_2$. When the reaction was followed by ^{31}P nmr spectroscopy, the presence of trans-$[Pt(C{\equiv}CPh)I(PMePh_2)_2]$ was detected. This would suggest that a mechanism analogous to that represented by eqns (3.41) to (3.44) operated with the formation and reaction of $[Cu(C{\equiv}CPh)]$. This is also likely to be the mechanism for other reported CuI catalysed isomerisations[21a,b]. The isomerisation of cis-$[Pt(C{\equiv}CPh)_2(PBu_3)_2]$ catalysed by CuI has been investigated by Sonogashira and Hagahari[107]. In acetone a 1:1 adduct between the cis-Pt complex and CuI was isolated as a white crystalline material (eqn. 3.44a). When passed through an alumina chromatographic column a mixture of cis and trans bis-(ethynyl) complexes was formed. The

$$\text{cis-}[Pt(C{\equiv}CPh)_2(PBu_3)_2]+CuI \xrightarrow[\text{acetone}]{\text{room temp.}} \begin{matrix} Bu_3P & C{\equiv}CPh \\ & Pt \quad\quad CuI \\ Bu_3P & C{\equiv}CPh \end{matrix} \qquad (3.44a)$$

intermediacy of trans-$[Pt(C{\equiv}CPh)I(PBu_3)_2]$ in the isomerisation was also proposed as well as intermediates containing Cu-acetylene π bonds (eqn. 3-44a). In diethylamine the rate of isomerisation of cis-$[Pt(C{\equiv}CPh)_2L_2]$ depended on the phosphine with the rate decreasing as L = PMe_3>>$PPhBu_2$>PEt_3>PBu_3. The type of catalyst CuX also affected the rate, although to a lesser extent, with the rate decreasing as X = I>Br>Cl. The initial rate of isomerisation was found to be 1st order with respect to CuI.

Ph_3PCuCl catalyses the present isomerisation but very slowly with only 30% of the starting material being consumed after 15 days. The lowering of the reaction rate is likely to be due to the lower reactivity of the phosphine stabilised intermediate $[Cu(C{\equiv}CPh)(PPh_3)]$ compared with $Cu(C{\equiv}CPh)$ (from CuI) or $Hg(C{\equiv}CPh)_2$ (from HgX_2). Interestingly CuCl has no effect on cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ although this halide is highly insoluble in $CDCl_3$ and so less likely to react.

The gold complex $[AuCl\{P(p\text{-}tol)_3\}]$ also had no effect on cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. This failure is presumably due to the unfavourable equilibrium in the reaction analogous to eqn. (3.41) and it has already been shown that ethynyls transfer quantitatively from gold to platinum (see 2-4.3f & 3.5.1f). It should be noted however that when cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ was prepared from cis-$[PtCl_2(PMe_2Ph)_2]$ and $[Au(C{\equiv}CPh)(PPh_3)]$, it subsequently isomerised to trans (see 3.5.1f) and gold intermediates may play a part in this isomerisation. (PMe_2Ph complexes though do exhibit a greater tendency for trans geometry and the reaction is slow (4 days) so it cannot be said for certain whether this is the case).

As mentioned in section 3.3 tin ethynyls have been used in the preparation of platinum ethynyls, and so the effect of tin halides was investigated. Anhydrous tin(II) chloride (0.2 mol equivalent) slowly

caused isomerisation of the cis-bis(ethynyl) with the reaction being 70% complete after 15 days. On the other hand tin(IV)chloride reacted irreversibly with the cis-bis(ethynyl) producing trans-[Pt(C≡CPh)Cl-$(PMePh_2)_2$] and cis-$[PtCl_2(PMePh_2)_2]$, consuming 50% of the starting material in 24 hours. With $SnCl_4$ the stoichiometry was difficult to control and the exact ratio of Sn:Pt was difficult to determine, although there was enough chloride to convert the ethynyl completely to the platinum dihalide. Reverse transfer of the ethynyl from tin(IV) as $[SnMe_3(C\ CPh)]$[90b,d] and $[SnMe_2(C\ CPh)_2]$[90c] to platinum have both been used in the preparation of Pt ethynyls.

3.5.3 Isomerisation of cis$[Pt(p\text{-}tol)_2(PPh_3)_2]$ by $HgCl_2$.

To compare the effects of HgX_2 on platinum bis(ethynyls) with other bis(organo)platinum systems, the reactions of the bis(aryl) species $[Pt(p\text{-}tol)_2(PPh_3)_2]$ (p-tol = para-methylphenyl) with $HgCl_2$ were investigated. Unlike the ethynyls the starting cis isomer is the stable isomer (the trans isomer for this compound, or the very similar $[PtPh_2(PPh_3)_2]$ being unknown). Both forms of the mono(aryl)intermediate $[Pt(p\text{-}tol)Cl(PPh_3)_2]$ have been isolated and their ^{31}P nmr parameters determined[103].

When 0.1 molar equivalents of $HgCl_2$ was added to a $CDCl_3$ solution of cis-$[Pt(p\text{-}tol)_2(PPh_3)_2]$ there was immediate growth of cis-[Pt(p-tol)-$Cl(PPh_3)_2$] (δ20.8, J 1563 ; δ17.6, J 4577 ; $^2J_{PP}$ 14Hz) followed by a slower growth of the trans-mono(aryl) (δ24.1, J 3167) however, after 2 days the total extent of reaction was <10%. Increasing the amount of $HgCl_2$ to 10 molar equivalent increased the quantity of both the mono(aryl) isomers but there was no sign of any trans-bis(aryl) species, and even after 2 days there was still a trace of cis-$[Pt(p\text{-}tol)_2)PPh_3)_2]$ although after 5 days there was only a mixture of cis and trans mono(aryl)

species in solution. Addition of one molar equivalent of $[Hg(\underline{p}\text{-tol})_2]$ to this solution resulted in the slow consumption of the cis isomer over 2 days and ^{31}P nmr spectroscopy showed only trans-$[Pt(\underline{p}\text{-tol})Cl(PPh_3)_2]$ and a very weak signal at δ14.2 (too weak for platinum satellite signals to be visible) which may be due to a trace of trans-$[Pt(\underline{p}\text{-tol})_2(PPh_3)_2]$ or else cis-$[PtCl_2(PPh_3)_2]$ (δ14.3 J 3673) arising from slow decompostion of the aryl complexes. So again the mercury complex seems to be reacting as described in eqns.(3.41 - 3.44), although the analagous reaction to eqn (3.42) need not operate and the equilibrium of the analogue of eqn.(3.44) lies well over to the left hand side. Indeed when 0.5 molar equivalents of $HgCl_2$ were added to cis-$[Pt(\underline{p}\text{-tol})_2(PPh_3)_2]$ after 5 days all the starting material had been consumed indicating that both halides could transfer from Hg to Pt (eqn. 3.45)

$$2\underline{cis}\text{-}[Pt(\underline{p}\text{-tol})_2(PPh_3)_2]+HgCl_2 \longrightarrow 2\underline{trans}\text{-}[Pt(\underline{p}\text{-tol})Cl(PPh_3)_2]+[Hg(\underline{p}\text{-tol})_2] \qquad (3.45)$$

3.5.4 The nmr parameters of cis-$[Pt(C{\equiv}CPh)_2ClL]$

From tables 3.3 and 3.4 it can be seen that the magnitude of $^1J_{PPt}$ is indicative of the group trans to the phosphine. This well known phenomenon has been related to the trans-influence of the ligand trans to the phosphine. Ligands with high σ-bonding ability will weaken the s-character of the Pt-P bond and so reduce the coupling constant, as $^1J_{PtP} \propto a^2_{Pt}$ where a is the s-character of the hybrid orbital used by Pt in the P-Pt bond. So for L = $PMePh_2$, a phosphine trans to ethynyl has a PPt coupling constant ∿2,300Hz, trans to phosphine of ∿2550Hz and trans to chloride ∿3600Hz, due to the trans effect of these ligands decreasing in the order : ethynyl>phosphine>halide. In the complex

cis-[Pt(C≡CPh)Cl($PMePh_2$)$_2$], the two PPt coupling constants are 2325 and 3672 Hz, typical values for a phosphine trans to an ethynyl and a chloride respectively. Similarily for [Pt(C≡CPh)Cl(dptpe)] the PPt coupling constants follow the expected pattern. With triphenylphosphine, though, the situation is very different with a very large value (4441Hz) for phosphine trans to halide compared with, for example, cis-[Pt(PPh_3)$_2$$Cl_2$] ($^1J_{PPt}$ 3673). Similarily the coupling constant for the phosphine trans to ethynyl is small ($^1J_{PPt}$ 1755). The same effect was seen in the bromo complex cis-[Pt(C≡CPh)Br(PPh_3)$_2$] and these ranges of values are typical for the cis-mono(aryl)complexes (e.g. cis-[Pt(p-tol)Cl(PPh_3)$_2$] as shown in the previous section, J_{PtP} 4577 and 1563 Hz). It has been noted previously [108] that when a phosphine is trans to a group of low trans influence and cis to a group of high trans influence that J_{PPt} for P trans to halide can be very large. Clearly the situation is more complicated since $PMePh_2$ and dptpe give "normal" coupling constants and only PPh_3 is affected in this way. Furthermore in the complexes trans-[PtRCl(PPh_3)$_2$] (R=p-tol, C≡CPh), with the aryl ligand $^1J_{PPt}$ (P trans to P) is very large ($^1J_{PtP}$ 3167) whereas with the phenylethynyl the more "normal" values of 2661Hz is obtained. So the unusual parameters in cis-[Pt(C≡CPh)X(PPh_3)$_2$] cannot be solely explained by the cis effect of the ethynyl being similar to aryl when this is clearly not the case in trans-[Pt(C≡CPh)X(PPh_3)$_2$].

3.5.5 Nmr evidence for Hg-Pt adduct formation.

The introduction of metal halides into solutions of cis-[Pt(C≡CPh)$_2$($PMePh_2$)] usually caused a significant change in the ^{31}P nmr parameters of that complex. These changed parameters are shown in Table (3.5). It can be seen from the table that the magnitude of the shift in parameters increases as the relative amount of salt present

Table 3.5 Effects of metal salts on ^{31}P nmr parameters.

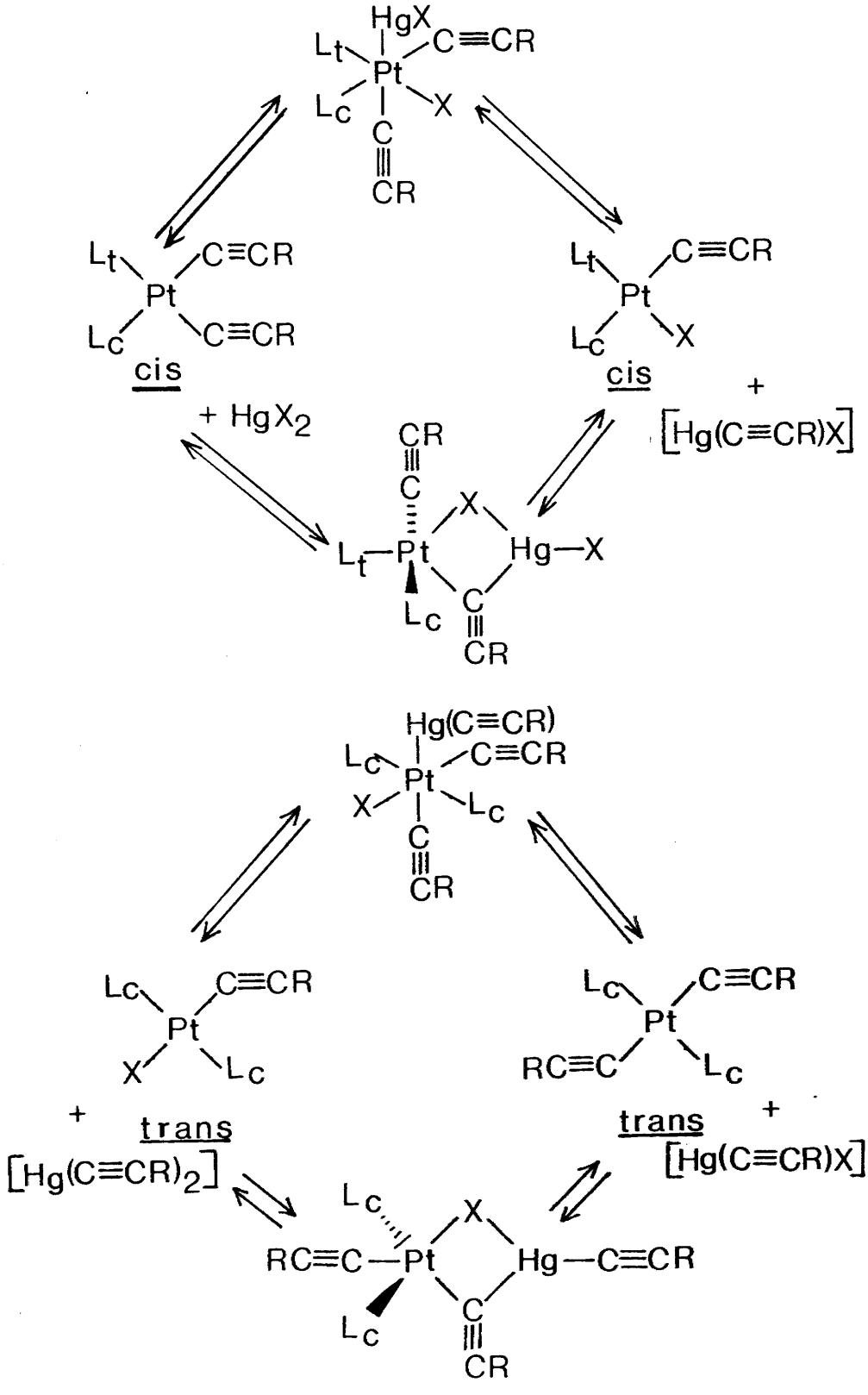
Ethynyl Complex	Salt	ratio	δp	$\Delta\delta p$	J_{PtP}	ΔJ_{PtP}
cis-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$	-	-	-2.0		2289	
	$HgCl_2$	10:1	-2.9	0.9	2378	89
		2:1	-3.3	-1.3	2420	131
	$HgBr_2$	10:1	-2.4	-0.4	2318	29
		1:1	-2.6	-0.6	2336	47
	HgI_2	10:1	-3.1	-1.1	2375	86
		5:1	-4.2	-2.2	2450	161
	$[Hg_2Cl_6]^{2-}$	10:1	-2.3	-0.3	2324	35
	PhHgCl	10:1	-2.0	0	2306	17
	CuI	10:1	-2.0	0	2308	19
	Ph_3PCuCl	10:1	-2.2	-0.2	2316	27
	$SnCl_2$	10:1	-2.0	0	2298	9
cis-$[Pt(C\equiv CPh)_2(PPh_3)_2]$	-	-	16.7		2328	
	$HgCl_2$	5:1	16.7		2359	31
		2:1	16.5	-0.2	2337	9
		1:1	13.4	-3.3	2491	162

increases. The effects are largest for HgX_2 and smallest for $SnCl_2$, the rate of isomerisation of the cis complex decreases in the same order. For the trans-bis and mono-ethynyls the effect of metal salts is much less pronounced with $^1J_{PPt}$ never varying by more than 10Hz from the values expected for the pure compounds. It is suspected that the large change in parameters for the cis complex is due to rapidly reversible adduct formation acting before the ligand exchange reactions. If this were the case then increasing the concentration of salt would move the time-averaged signal away from that expected for pure bis(ethynyl) towards that expected for the adduct. Also a stronger shift in parameters for a given ratio of platinum complex : salt (eg. $HgCl_2$ and HgI_2 compared with Ph_3PCuCl or $SnCl_2$ at a ratio of 10:1) would indicate a stronger interaction with a higher degree of adduct formation and hence a faster reaction rate. Finally,the change in magnitude of the parameter shift between cis and trans isomers would be expected as whether the mechanism is S_E2(cyclic) or oxidative addition/reductive elimination then, as shown in Fig. 3.3, the substitution reaction is at a ligand trans to a phosphine (L_t) in the cis isomer, and a ligand cis (L_c) to the phosphines in a trans isomer, and the effect would be expected to be largest when substitution occurs trans to phosphine.

3.6 Conclusions

Whilst it is clear that the factors controlling the relative stability of the cis-bis(phosphine)-bis(ethynyl)platinum complexes are complicated,for certain phosphines (PMe_2Ph) and ethynyls ($C{\equiv}CMe$) these complexes seem inaccessible. Even when such a geometry is accessible the actual isomer obtained depends heavily on the synthetic method and no one method for producing cis isomers is general. However the formation of cis isomers will depend on a rapid replacement of the second halide for ethynyl, or phosphine displacement of another ligand. The presence of

Figure 3.3 Possible transition states in HgX_2 catalysed isomerisations of $[Pt(C{\equiv}CR)_2L_2]$



metal halide salts, which catalyse the cis → trans isomerisation will also affect the products geometry and their use should be avoided if cis isomers are desired.

3.7 Experimental

The following compounds were prepared by literature methods $[PtCl_2(cod)]$[13], $[Au(C{\equiv}CPh)(PPh_3)]$ (see chapter 2), $[CuCl(PPh_3)]$[109], and $Hg(C{\equiv}CPh)_2$ [110] $[PtCl_2(dptpe)]$[111].

(1,5-Cyclooctadiene)bis(phenylethynyl)platinum:- To a suspension of $[PtCl_2(cod)]$ (0.5g, 1.34 mmol) in ethanol under N_2 and at 0^oC was added a freshly prepared mixture of $HC{\equiv}CPh$ (0.27g, 2.7 mmol) and NaOEt (prepared from adding 61.5 mg, 2.7 mmol of Na to 10ml EtOH) dropwise and with constant stirring. The resultant yellow solid was filtered off after 50 mins. affording crude $[Pt(C{\equiv}CPh)_2(cod)]$ (0.7g, 103% due to NaCl impurities). Re-crystallisation from boiling $CHCl_3$ led to decomposition but three recrystallisations from CH_2Cl_2 finally yielded pure $[Pt(C{\equiv}CPh)_2(cod)$ M.Pt 178 -97°C (dec) $\nu(C{\equiv}C)$ 2130cm^{-1}(w), 2135 cm^{-1}(sh) Found C,57.3 ; H, 4.2% ; required for $C_{24}H_{22}Pt$, C, 57.0 ; H 4.4%.

Cis-bis(methyldiphenylphosphine)bis(phenylethynyl)platinum:-

(a) From $[PtCl_2(PMe_2Ph_2)_2]$ - To a suspension of cis-$[PtCl_2(PMePh_2)_2]$ (0.5g, 0.75 mmol) in ethanol (20ml) at 0^oC was added $PhC{\equiv}CH$ (153mg, 1.5mmol followed immediately by NaOEt (prepared from 34.5mg (1.5mmol) Na in 5ml EtOH). The solid remained after 2 hrs stirring, after which filtration yielded crude product (440mg, 74%). Re-crystallisation from $CHCl_3$/pentane afforded pure cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ M.Pt. 172-3°C $(C{\equiv}C)$ 2120 cm^{-1}(w) 2130 cm^{-1}(sh). Found C,62.4 ; H 4.6%; required for $C_{42}H_{36}P_2Pt$, C, 63.2 ; H, 4.55%.

(b) From $[Pt(C\equiv CPh)_2(cod)]$ - To a solution of $[Pt(C\equiv CPh)_2(cod)]$ (500mg, 0.99 mmol) in CH_2Cl_2 (30ml) under N_2 was added a solution of $PMePh_2$ (350 µl; 1.98 mmol) in CH_2Cl_2 (10ml) over a period of 5 mins. After 15 mins stirring a clear, brown solution resulted. Removal of solvent left the crude product, recrystallised form $CHCl_2$/light petroleum (60-30°C) (314mg, 40%).

(c) From $[Pt(C\equiv CPh)_2(CO)(PMePh_2)]$ - To a solution of cis-$[PtCl_2(CO)(PMePh_2)]$ (0.2g, 0.4 mmol) in $CHCl_3$ (10ml) at 0°C under N_2 was added $Hg(C\equiv CPh)_2$ (163mg, 0.4 mmol) in $CHCl_3$ (5ml). The mixture was stirred for 2 mins then $[Et_4N]Cl$ (67mg, 0.4mmol) was added. Stirring was continued for 5 mins, during which time a grey precipitate of $(Et_4N)_2(Hg_2Cl_6)$ formed. This was removed by rapid filtration leaving cis-$[Pt(C\equiv CPh)_2(CO)(PMePh_2)_2]$ in the orange solution. $PMePh_2$ (87µl, 0.4mmol) was immediately added to the solution which was stirred for 5 mins. Removal of solvent yielded cis-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$ (303mg, 94%)

Cis-bis(phenylethynyl)bis(triphenylphosphine(platinum:-

(a) From $[Pt(C\equiv CPh)_2(cod)]$- To a solution of $[Pt(C\equiv CPh)_2(cod)]$ (185mg, 0.37mmol) in CH_2Cl_2 (20ml) at 0°C under N_2 was added Ph_3P (182mg, 0.69mmol) in CH_2Cl_2 (5ml). The solution was stirred for 15 mins during which time a brown colour developed. After filtration and concentration crude product was isolated (267mg, 79%). Re-crystallisation from CH_2Cl_2/ pentane gave initially trans-$[Pt(C\equiv CPh)Cl(PPh_3)_2]$ by-product (M.Pt. 210-212°C, $\nu(C\equiv C)$ 2130 cm^{-1} $\nu(Pt-Cl)$ 315 cm^{-1} J_{PtP} 2665 Hz) followed by the desired cis-$[Pt(C\equiv CPh)_2(PPh_3)_2]$ M.Pt. 210-212°C (lit[89a] 206-8°C) $\nu(C\equiv C)$ 2110 cm^{-1} J_{PtP} 2329 Hz.

(b) From $[PtCl_2(CO)(PPh_3]$ - cis-$[PtCl_2(CO)(PPh_3)]$ (20mg, 38 μmol) was dissolved in $CDCl_3$ (0.5ml) and $[Au(C{\equiv}CPh)(PPh_3)]$ (10.3mg, 72 μmol) was added. After 15 mins, ^{31}P nmr spectroscopy showed signals for $[AuCl(PPh_3)]$ (δ33.2) and cis-$[Pt(C{\equiv}CPh)_2(CO)(PPh_3)]$ (δ12.5, J_{PPt} 2162). PPh_3 (9.6mg, 37μmol) was added, and ^{31}P nmr spectroscopy showed that cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ had formed (δ16.7 J_{PPt} 2330) and a broad signal (∿δ34) due to phosphine exchange with $[AuCl(PPh_3)]$.

Cis-(methyldiphenylphosphine)(triphenylphosphine)bis(phenylethynyl)platinum:

To a solution of cis-$[PtCl_2(CO)(PMePh_2)]$ (20mg, 40.5μmol) in $CDCl_3$ (0.5ml) was added $[Au(C{\equiv}CPh)(PPh_3)]$ (45.3mg, 80.9μmol). After 15 mins, cis-$[Pt(C{\equiv}CPh)_2(CO)(PMePh_2)]$ (δ-3.0 J_{PtP} 2082) had formed. Addition of PPh_3 (11.1mg, 42μmol) led to rapid evolution of CO and a complicated nmr spectrum occurred containing signals for cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$, cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ and a set of signals (see Table 3.3) assigned to cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)(PPh_3)]$, the relative ratio of the 3 species being 1:1:2.

Attempted prep. of cis-$[Pt(C{\equiv}CH)_2(PMePh_2)_2]$. C_2H_2 gas was passed through a suspension of cis-$[PtCl_2(PMePh_2)_2]$ (300mg, 4.5mmol) at 0°C. After a few minutes NaOEt (from Na(20.7mg, 0.9mmol) in 5ml EtOH) was added. The solution was stirred for 2 hrs leaving a brown solution with no solid material present. Solvent was removed and the crude product re-dissolved in $CDCl_3$. ^{31}P nmr spectroscopy showed a large singlet (δ29.1) and no evidence of phosphine platinum species. Proton nmr did not show the presence of an ethynyl proton.

Attempted prep. of cis-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$:- The reaction was performed under identical conditions to the above experiment except that propyne was used instead of ethyne. At the end of the reaction an orange solution remained where nmr in $CDCl_3$ showed a large singlet at δ29.8 and unreacted $[PtCl_2(PMePh_2)_2]$.

Attempted prep. of cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$:- via NaOEt - When a suspension of cis-$[PtCl_2(PMe_2Ph)_2]$ in EtOH was treated with HC≡CPh and NaOEt for 2 hrs at 0°C, the main product of the reaction was starting material (δ-18.2 J_{PtP} 3379). To investigate the reaction, four samples of cis-$[PtCl_2(PMe_2Ph)_2]$ (each 75mg in 10ml EtOH) were treated with 1ml of a standard solution of HC≡CPh (282mg in 10ml EtOH) and 0.5ml of a standard solution of NaOEt (128mg Na in 10ml EtOH). The reactions were allowed to proceed for 2hrs at 0°C, 20°C and 60°C and 24 hrs at 20°C, at the end of which solvent was removed in vacuo and the crude product re-dissolved in $CDCl_3$ and their ^{31}P nmr spectra recorded. (See Table 3.2) In none of the reactions had cis-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ formed.

{1,2-bis(di-p-tolylphosphino)ethane}bis(phenylethynyl)platinum:- (a) via NaOEt - To a suspension of $[PtCl_2(dptpe)]$ (500mg,0.7mmol) in EtOH at 0°C was added HC≡CPh (142mg, 1.4mmol) followed by NaOEt (from 32mg (1.4mmol)Na). After two hours stirring a dark brown solution had formed which contained mainly $PtCl_2(dptpe)$, Excess NaOEt and HC≡CPh were added, and the solution refluxed for 30 mins. The main product was now $[Pt(C{\equiv}CPh)_2(dptpe)_2]$ identified from its ^{31}P nmr parameters (see Table 3.3) along with several unidentified impurities.

(b) via $Hg(C{\equiv}CPh)_2$ - $[PtCl_2(dptpe)]$ (30mg, 42μmol) was dissolved in $CDCl_3$ and $Hg(C{\equiv}CPh)_2$ (16.8mg, 42μmol) was added followed by Et_4NCl (6.4mg, 42μmol). The insoluble byproduct was removed by filtration and ^{31}P nmr spectroscopy showed that the main product was $[Pt(C{\equiv}CPh)_2$-(dptpe)] along with some [Pt(C≡CPh)Cl(dptpe)].

Trans-bis(methyldiphenylphosphine)bis(phenylethynyl)platinum:- (a) via CuI catalysed reaction - To a suspension of cis-$[PtCl_2(PMePh_2)_2]$ (0.2mg, 0.3mmol) in $NHEt_2$ (25ml) were added PhC≡CH (71.4mg 0.7mmol) and CuI (11mg, 57μmol). The mixture was refluxed for 10 mins, and the solvent reduced at low pressure. Re-crystallisation of the white solid from $CHCl_3$/ethanol yielded trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ (136mg, 57%). I.r. (ν(C≡C) 2110cm^{-1}) and nmr (see Table 3.3) parameters were consistent with literature values for trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$[88c].

(b) Via $Hg(C{\equiv}CPh)_2$ - To a solution of cis-$[PtCl_2(PMePh_2)_2]$ (20mg, 30μmol) was added $Hg(C{\equiv}CPh)_2$ (25.6mg, 64μmol). After 30 mins. the solution was filtered to remove [Hg(C≡CPh)Cl] and ^{31}P nmr spectroscopy showed that trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ was the main product with some (10%) trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$.

(c) Via[Au(C≡CPh)(PPh_3)] - When two equivalents of [Au(C≡CPh)(PPh_3)] were added to $[PtCl_2(PMePh_2)_2]$ and the reaction monitored by ^{31}P nmr spectroscopy, trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ grew in, followed by a slow growth of trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. On one occasion a rapid growth of cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ was observed. If the reaction was performed in the presence of S_8 the cis-bis(ethynyl) was formed. All these reactions were performed in $CDCl_3$ (0.5ml) with 20mg of cis-$[PtCl_2(PMePh_2)_2]$ and 34mg of [Au(C≡CPh)(PPh_3)] and all reactants and products were soluble.

(d) By method (a) with less PhC≡CH - When method(a)was performed with 300mg (~45mmol) of cis-$[PtCl_2(PMePh_2)_2]$ and HC≡CPh (46.6mg, 0.46mmol) i.e. a 1:1 mole ratio, then after reflux in Et_2NH with a trace of CuI catalyst the product was a 1:1 mixture of starting material and trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ remained with a trace of trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$.

Trans-bis(methyldiphenylphosphine)bis(propynyl)platinum:- (a) Via $[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ cis-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ was prepared from cis-$[PtCl_2(CO)(PMePh_2)_2]$, $Hg(C{\equiv}CMe)_2$ and Et_4NCl by the literature method[54] One equivalent of $PMePh_2$ was added and the solution stirred for 5 mins. Solvent removed to give the crude product (633.5mg, 78%). Re-crystallisation from acetone gave pure trans-$[Pt(C{\equiv}CMe)_2(PMePh_2)]$ (498mg, 57%) M.Pt. 176-8°C, $\nu(C{\equiv}C)$ 2130 cm^{-1}. Nmr parameters as in Table 3.2. Found C, 56.8; H, 4.60; P, 9.23%: required for $C_{42}H_{36}P_2Pt$: C, 57.06 ; H, 4.79 ; P, 9.2%. When the reaction was followed by nmr, adding the phosphine in three separate portions, cis-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$ was formed in good yield (maximum 32%) but it isomerised rapidly (~10 mins) to the trans form.

(b) Via $[Hg(C{\equiv}CMe)_2]$. To a solution of $[PtCl_2(PMePh_2)_2]$ (20mg, 30μmol) in $CDCl_3$ (0.5ml) was added $Hg(C{\equiv}CMe)_2$ (17mg, 62μmol). The solution was allowed to stand overnight and filtered, leaving a solution of trans-$[Pt(C{\equiv}CMe)_2(PMePh_2)_2]$ (identified by its spectroscopic parameters).

Trans-bis(dimethylphenylphosphine)bis(phenylethynyl)platinum:- (a) From $Pt(C{\equiv}CPh)_2(cod)$ - To a CH_2Cl_2 solution of $[Pt(C{\equiv}CPh)_2(cod)]$ (700mg, 1.4mmol) was added PMe_2Ph (376μl, 2.6mmol), under N_2 at 0°C. The solution was stirred for 30 mins, filtered and solvent removed. 2 successive recrystallisations from $CHCl_3$/pet.ether (60-80°C) gave yellow crystals of trans-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ (46%). I.r. and n.m.r parameters agreed with literature values[57].

(b) From $[Pt(C{\equiv}CPh)_2(CO)(PMe_2Ph)]$ - To a solution of cis-$[Pt(C{\equiv}CPh)_2(CO)(PMe_2Ph)]$ (prepared from $[PtCl_2(CO)(PMe_2Ph)]$ (1g, 2.3mmol), $Hg(C{\equiv}CPh)_2$ and Et_4NCl) in $CHCl_3$ (50ml) under N_2 was added 330µl (2.3mmol) of PMe_2Ph. After five minutes stirring the orange solution was filtered to remove a grey precipitate. The solution was concentrated and light petroleum (60-80°C) added until crystallisation just began. The first product was white crystals of the mercury by-product, followed by yellow crystals of trans-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$ (856mg, 55%).

(c) Via $[Au(C{\equiv}CPh)(PPh_3)]$ - To a $CDCl_3$ (0.5ml) solution of cis-$[PtCl_2(PMe_2Ph)_2]$ (20mg, 37µmol) was added $[Au(C{\equiv}CPh)(PPh_3)]$ (41mg, 73µmol). A rapid depletion of $[Au(C{\equiv}CPh)(PPh_3)]$ took place and a mixture of cis and trans-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)]$ and trans-$[Pt(C{\equiv}CPh)Cl(PMe_2Ph)_2]$ was formed (see Tables 3.3 and 3.4 for spectroscopic parameters). After 4 days standing at room temperature the main product was trans-$[Pt(C{\equiv}CPh)_2(PMe_2Ph)_2]$.

Trans-bis(dimethylphenyl)bis(ethynyl)platinum:- To 252mg (0.46mmol) of $[PtCl_2(PMe_2Ph)_2]$ in Et_2NH (25ml) was added 10mg of CuI. C_2H_2 gas was bubbled through the solution for 2 hrs at 0°C. The solution was filtered and solvent removed leaving crude trans-$[Pt(C{\equiv}CH)_2(PMe_2Ph)_2]$, whose nmr and ir parameters were identical to literature values[57].

Trans-chlorobis(methyldiphenylphosphine)(phenylethynyl)platinum:-
(a) cis-$[PtCl_2(PMePh_2)_2]$ (503 mg, 7.6mmol) and $[Hg(C{\equiv}CPh)_2]$ (305mg, 7.6mmol) were stirred together in $CHCl_3$ (25ml) for 1 hr. The orange solution was filtered to remove $[Hg(C{\equiv}CPh)Cl]$ and solvent removed under reduced pressure. The crude product (561mg) was recrystallised from $CHCl_3$/pentane to give pure product as white crystals (352mg, 64%).

M.Pt. 213-4°C Found : C,55;4;H 4.1; P8.3: required for $C_{34}H_{31}ClP_2Pt$, C,55.8, H.4.3; P, 8.5%. ir $\nu(C\equiv C)$ 2130 cm^{-1}., $\nu(Pt-Cl)$ 315 cm^{-1}.

(b) If the above preparation was repeated with 29mg (43μmol) of cis-$[PtCl_2(PMePh_2)_2]$ and 8.7mg (21.6μmol) of $Hg(C\equiv CMe)_2$ and after mixing in $CDCl_3$ (0.5ml), Et_4NCl (3.6mg, 21.7μmol) was added then immediately after filtration along with cis-$[Pt(C\equiv CPh)_2(PMePh_2)_2]$, trans-$[Pt(C\equiv CPh)Cl(PMePh_2)_2]$ and trans-$[Pt(C\equiv CPh)Cl(PMePh_3)_2]$ a small pair of doublets (δ3.6, J_{PtP}2325; δ-4.8, J_{PtP}3672 ; $^2J_{PP}$ 18Hz) assigned to cis-$[Pt(C\equiv CPh)Cl(PMePh_2)_2]$. After 20 minutes standing at room temperature only trans-$[Pt(C\equiv CPh)Cl(PMePh_2)_2]$ remained.

Trans and cis-chlorobis(triphenylphosphine)(phenylethynyl)platinum:- If the preceding reaction was repeated with cis-$[PtCl_2(PPh_3)_2]$ (30mg, 40μmol), $Hg(C\equiv CPh)_2$ (7.4mg, 18.4μmol) and Et_4NCl (3.0mg, 13.1μmol) then after filtration, ^{31}P nmr spectroscopy showed the presence of cis-$[PtCl_2(PPh_3)_2]$, and two complexes, a pair of doublets (δ18.6, J_{PtP} 1755 ; δ14.9, J_{PtP} 4441; $^2J_{PP}$ 17.3 Hz) assigned to cis-$[Pt(C\equiv CPh)Cl(PPh_3)_2]$ and a singlet (δ21.5, J_{PtP} 2663) which steadily grew in and was assigned to trans-$[Pt(C\equiv CPh)Cl(PPh_3)_2]$. The assignment was confirmed when the same sets of signals were seen in the $HgCl_2$ catalysed isomerisation of cis-$[Pt(C\equiv CPh)_2(PPh_3)_2]$.

Trans-chlorobis(methyldiphenylphosphine)(methylethynyl)platinum:- To $[PtCl_2(PMePh_2)_2]$ (20mg, 30.0μmol) in $CDCl_3$ (0.5ml) was added $Hg(C\equiv CMe)_2$ (7.3mg, 26.4μmol). The mixture was allowed to stand overnight and then filtered. Nmr parameters (see Table 3.4) were consistent with trans-$[Pt(C\equiv CMe)Cl(PMePh_2)_2]$.

Isomerisation reactions:- These were all performed on an nmr scale experiment, typically with 20mg of the cis-bis(ethynyl) or cis-bis(aryl) complex in the minimum amount of $CDCl_3$(0.5ml) (or occasionally thf or toluene) and the appropriate amount of catalyst (usually 0.1 mol equivalents) added as a solid or in solution. The reactions were followed by ^{31}P nmr spectroscopy. The main results are given in the text (section 3.5.2)

(a) Isomerisation of cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$

(i) Effect of heat : A solution of the complex was heated until boiling for 5 minutes. On cooling there was no change in the nmr spectrum.

(ii) Effect of $PMePh_2$: On addition of $PMePh_2$ (0.08 mol equiv) to a solution of the complex caused no change in the nmr spectrum even on standing for 24 hrs. Increasing the amount of $PMePh_2$ produced signals for free and oxidised phosphine but no isomerisation.

(iii) Effect of $[Bu_4N]I$: This catalyst also had no effect on the complex even after 24 hrs.

(iv) Effect of $HgCl_2$: If in $CDCl_3$ then immediately after addition signals for cis-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ were evident, followed rapidly by trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$. After 10 mins trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$ was detected and this psecies grew in steadily until after 3 hrs it was the main product (90%) with 10% of the trans-mono(ethynyl) remaining.

In toluene, the reaction proceeded at a similar rate and again trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ was detected before any trans-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$. No cis-mono(ethynyl) was detected in this case.

In thf (tetrahydrofuran) the reaction was similar except that the product was formed as a precipitate and the reaction was faster than in either $CDCl_3$ or toluene.

(v) Effect of other Hg salts : $HgBr_2$ and HgI_2 were just as effective as $HgCl_2$ in catalysing the isomerisation, although in neither case was any cis-$[Pt(C{\equiv}CPh)X(PMePh_2)_2]$ detected $[Et_4N]_2[Hg_2Cl_6]$ was also just as rapid in causing the isomerisation, as was [Hg(C≡CPh)Cl] but [HgPhCl] did not cause any isomerisation even after 24hrs.

(vi) Effect of CuI : On addition of CuI a slow isomerisation took place. After 48 hours only trans-bis-and mono-ethynyl complexes remained. During isomerisation broad peaks were observed and the trans-bis(ethynyl) peak remained broadened probably due to association of the CuI catalyst with the platinum ethynyl.

(vii) Effect of other Cu salts : CuCl failed to catalyse any isomerisation in a 24 hr time period. $[CuCl(PPh_3)]$ did catalyse the isomerisation very slowly with 33% product after 15 days.

(viii) Effect of Sn chlorides : $SnCl_2.2H_2O$ was dried in vacuo for 2 hrs at 100°C during which time the sample of 1.5090g lost 267 mg (would expect to lose 240 mg if formula is correct). The dried $SnCl_2$ caused slow isomerisation with the reaction being 50% complete after 15 days. $SnCl_4$ also reacted with the complex but addition of 0.3 equiv. produced only trans-mono-(ethynyl) and cis-$[PtCl_2(PMePh_2)_2]$ although after 44 hrs the main product was still cis-$[Pt(C{\equiv}CPh)_2(PMePh_2)_2]$.

(ix) Effect of Pt ethynyls : Addition of trans-$[Pt(C{\equiv}CPh)Cl(PMePh_2)_2]$ to pure cis-bis(ethynyl) produced no reaction after 24 hrs. This rules out the isomerisation proceeding through a series of Pt ethynyl/chloride exchanges.

(x) Effect of $[AuCl(PPh_3)]$: there was no reaction between the complex and $[AuCl(PPh_3)]$ even after 24 hrs standing.

(b) Isomerisation of cis-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$

(a) Effect of $HgCl_2$: Addition of 0.2 equiv. of $HgCl_2$ to a sample of the complex in $CDCl_3$ brought about initial broadening of the bis(ethynyl) signal. After 30 mins signals for both cis and trans isomers of both bis-and mono-(ethynyls) could be detected. After 24 hrs only 75% of the starting material head reacted. When repeated with one equiv. of $HgCl_2$ the signal for cis-$[Pt(C{\equiv}CPh)Cl(PPh_3)_2]$ was very strong (70%) but on standing for 24 hrs the main product was cis-$[PtCl_2(PPh_3)_2]$ due to decomposition.

(b) Effect of $HgBr_2$: On addition of 0.1 equiv. $HgBr_2$ (added in EtOH solution) a complex spectrum resulted containing no signal for starting material but signals for cis and trans-$[Pt(C{\equiv}CPh)Br(PPh_3)_2]$, trans-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ and two unidentified signals at δ13.7, J 3531 and δ21.6 J 2656 assigned by analogy to the above reaction to cis and trans-$[PtBr_2(PPh_3)_2]$ respectively.

(c) Effect of HgI_2 : 30 mins after addition of HgI_2 signals for trans-bis and mono-ethynyls were detectable but there was no evidence for any of the dihalides being present.

(c) Reactions of cis-$[Pt(p\text{-}tol)_2(PPh_3)_2]$ with $HgCl_2$

When 0.1 equiv of $HgCl_2$ was added to $[Pt(p\text{-}tol)_2(PPh_3)_2]$, there was immediate production of cis-mono(aryl)complex followed by the trans isomer. The reaction was very slow, with only 3% of the starting complex being present after 2 hrs. Increasing the amount of $HgCl_2$ to 0.5 equiv. after 7 days, the main product was trans-$[Pt(p\text{-}tol)Cl(PPh_3)_2]$. Addition

of 1 equivalent of [$Hg(p\text{-}tol)_2$] and heating to 50°C for 2 hrs converted the mixture to <u>trans</u>-[$Pt(p\text{-}tol)Cl(PPh_3)_2$] but no <u>trans</u>-bis(aryl) could be detected.

Chapter 4 - THE SYNTHESES AND REACTIONS OF AMINE, AMINOCARBENE AND IMINE COMPLEXES OF Pt(II)

4-1 - Introduction

Platinum carbene complexes, in some ways, show a similar history to the platinum olefin complexes mentioned in Chapter 1. $K[PtCl_3(C_2H_4)]$ represents the first metal olefin complex (and the first organometallic complex) to be prepared[1] although it took a long time for its true structure to be understood[2]. In a similar vein, the first preparation of a platinum carbene (indeed of any metal-carbene complex) was reported by Chugaev and Skanawy-Grigorjowa in 1915 [112] who treated $[Pt(CNMe)_4]^{2+}$ with hydrazine. Again it took a long period of time (until 1970) before this complex was recognised as a cyclic platinum carbene,[113] with the X-ray crystal structure finally being determined for both Chugaev's salt[114] and its Pd analogue[113a] (eqn. 4-1). Hydroxylamine and methylhydrazine

$$[Pt(CNMe)_4]^{2+} + H_4N_2 \longrightarrow \left[\begin{array}{c} H \\ | \\ N-N \\ \| \\ Me-N-C \quad C-N-Me \\ \quad H \quad\quad\quad H \\ \quad\quad Pt \\ \quad MeNC \quad\quad CNMe \end{array}\right]^{+} + H^{+} \qquad (4\text{-}1)$$

react in an analogous manner to form carbenes with the ligand framework MeHN-C̈=N-O-C̈-NHMe and MeHN-C̈-N(Me)-N=C̈-NHMe respectively[113b,115].

In the period between the initial preparation of Chugaev's salt and its characterisation the field of metal carbene chemistry had grown enormously as can be seen from several review articles dating from this period.[116] This growth was stimulated by the first planned synthesis of a metal carbene by Fischer and Maasbol in 1964[117] (eqn.4-2). The first report of a characterised Pt carbene came from Chatt and Richards in 1969[118] who

$$W(CO)_6 + LiR \longrightarrow [W(CO)_5\{C(R)OLi\}] \xrightarrow{[Me_3O]^+} [W(CO)_5\{C(R)OMe\}] \qquad (4\text{-}2)$$

found that the treatment of co-ordinated isocyanides with alcohol would give addition across the C=N band, giving a carbene product (eqn. 4-3). Many other methods have been used to make platinum(II) carbenes, and in a few cases Pt(IV) carbenes, although as yet no Pt(0) carbenes have been

$$\underline{\text{Cis}}\text{-}[PtCl_2(CNPh)(PEt_3)] + EtOH \longrightarrow \underline{\text{cis}}\text{-}[PtCl_2\{C(NHPh)OEt\}(PEt_3)] \quad (4\text{-}3)$$

isolated. A brief survey of these methods is given in the next section.

4-2. - Synthetic routes to Pt(II) carbenes.

(a). Synthesis from organoplatinum precursors.

i) Alcohols[118] amines[115,119] and thiols[115] can all attack co-ordinated isocyanide complexes to produce carbenes in a manner analogous to eqn. (4-3). This method has been employed to prepare the unusual percarbene complex, $[Pt\{C(NHMe)_2\}_4]^{2+}$ (eqn. 4-4)[115a]:-

$$[Pt(CNMe)_4]^{2+} + 4NH_2Me \longrightarrow [Pt\{C(NHMe)_2\}_4]^{2+} \quad (4\text{-}4)$$

(ii) Nucleophilic attack on co-ordinated acetylenes has proven very successful. Starting from electroneutral monomeric complexes, and cationic carbene complexes were obtained[120] (eqn. 4-5). Anderson/Cross [121] modified the procedure by starting with halide bridged complexes which produced neutral carbene complexes[121] (eqn. 4-6).

$$\underline{\text{trans}}\text{-}[PtCl(Me)(PR_3)_2] + R_2C_2 \xrightarrow{Ag^+/MeOH} \underline{\text{trans}}\text{-}[PtMe\{C(CMe)CHR_2\}(PR_3)_2]^+ \quad (4\text{-}5)$$

The mechanism for both reactions is thought to proceed via a re-arrangement of a co-ordinated acetylene to a vinylidene species

$$\tfrac{1}{2}[Pt_2Cl_4(PR_3)_2] + RC{\equiv}CH + R^1OH \longrightarrow \underline{\text{cis}}\text{-}[PtCl_2\{C(OR^1)(CH_2R)\}(PR_3)] \quad (4\text{-}6)$$

which then undergoes nucleophilic attack (eqn. 4-7). A further variation was introduced by Chisholm and Bell[57] who found that

$$[Pt_2X_4L_2] + HC{\equiv}CPh \longrightarrow [PtX_2L(\eta^2\text{-}HC{\equiv}CPh)] \longrightarrow [PtX_2L(=C=CHR)]$$

$$\downarrow R^1OH \qquad (4\text{-}7)$$

$$[PtX_2\{C(OR^1)(CH_2R)\}L]$$

the reaction would proceed starting from a co-ordinated acetylide which could be protonated and then undergo nucleophilic attack (eqn. 4-8) to give cationic alkoxycarbenes.

$$\underline{trans}\text{-}[PtCl(C{\equiv}CR)L_2] + HPF_6 + R^1OH \longrightarrow \underline{trans}\text{-}[PtCl\{C(OR^1)CH_2R\}L_2][PF_6] \qquad (4\text{-}8)$$

(iii) If a complex already contains a carbon to heteroatom double bond then protonation of the ligand can produce carbene complexes[122] (eqn. 4-9).

$$\underline{trans}\text{-}[PtX\{C(NR)(NHPh)\}(PEt_3)_2] \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underline{trans}\text{-}[PtX\{C(NHR)(NHPh)\}(PEt_3)_2]^+ \qquad (4\text{-}9)$$

b) Synthesis from metal carbenes

This heading covers a range of synthetic procedures including i) modification of the metal-ligand framework by ligand exchange, ii) modification of the carbene ligand and iii) transfer of the carbene ligand from one metal centre to another. All these pathways have the common property of starting from one metal carbene complex to produce new ones. Some examples are given below.

(i) Neutral alkoxy(organo) carbenes have been converted into cationic complexes by ligand exchange reactions, as long as the chloride ion which will react with the product is rapidly removed as its silver salt (eqn. 4-10)[123]. Into this category also come the

$$\underline{cis}\text{-}[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)] + PMe_2Ph + Ag^+ \longrightarrow \underline{trans}\text{-}[PtCl\{C(OMe)CH_2Ph\}(PMe_2Ph)_2]^+ + AgCl \qquad (4\text{-}10)$$

the oxidative addition reactions at the metal centre which have been used to prepare Pt(IV) carbene complexes (eqn. 4-11)[124].

$$\underline{cis}\text{-}\left[PtCl_2\{C(NHMe)_2\}(PEt_3)\right] + Cl_2 \longrightarrow \left[PtCl_4\{C(NHMe)_2\}(PEt_3)\right] \quad (4\text{-}11)$$

(ii) Amine attack at the carbene can cause displacement of an alkoxy group[125] although the reaction (eqn. 4-12) was found to be dependent on the size and concentration of the amine, as well as the nature of the trans ligand. (With bulky amines and X=Cl, acyl formation was favoured (eqn. 4-12). With cyclic carbenes the attack by amines led to ring opening, with non cyclic carbenes produced[125] (eqn. 4-13).

$$\underline{trans}\text{-}\left[PtX\{C(OMe)Me\}(PMe_2Ph)_2\right]^+ + NHR_2 \xrightarrow{X=Me,Cl} \underline{trans}\text{-}\left[PtX\{C(NR_2)Me\}(PMe_2Ph)_2\right]^+$$

$$\xrightarrow{X=Cl} \underline{trans}\text{-}\left[PtX(COMe)(PMe_2Ph)_2\right] + \left[R_2NHMe\right]^+ \quad (4\text{-}12)$$

$$\underline{trans}\text{-}\left[PtX\{CO(CH_2)_2CH_2\}(PMe_2Ph)_2\right] + NHR_2 \longrightarrow \underline{trans}\text{-}\left[PtX\{C(NR_2)(CH_2)_3OH\}(PMe_2Ph)_2\right]^+ \quad (4\text{-}13)$$

(iii) No platinum carbene complexes have been made via transference of a carbene ligand from another metal centre although this method has been used for other metals such as iron[126] and gold[127] to prepare carbene complexes not accessible by other routes (eqns. 4-14, 4-15). In view of the known reactions of gold ethynyls with platinum halides (see chapter 1) gold carbenes may act as

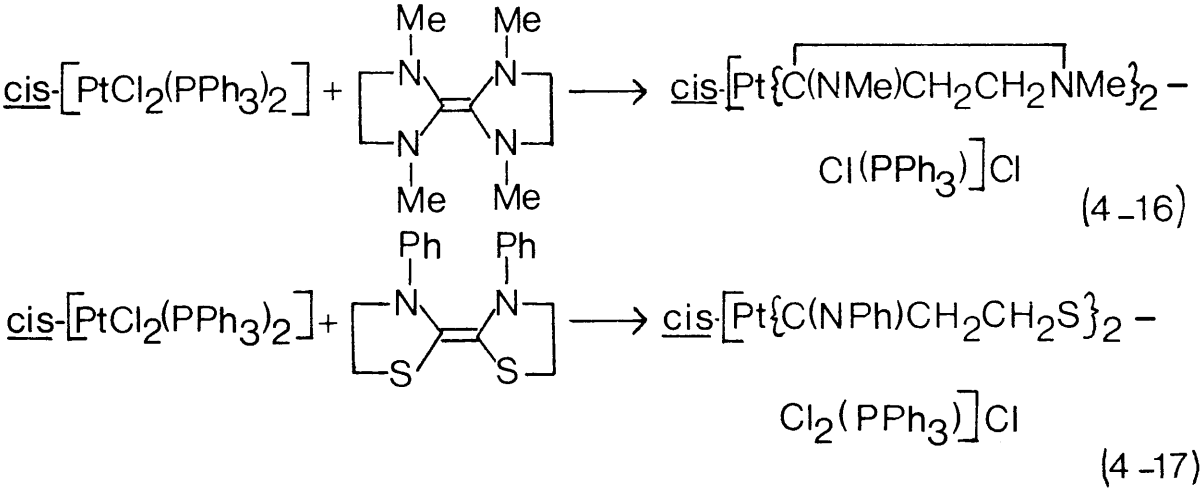
$$\left[MoCp(CO)\{C(OMe)Ph\}(NO)\right] + Fe(CO)_5 \xrightarrow{h\nu} \left[MoCp(CO)_2(NO)\right] + \left[Fe(CO)_4\{C(OMe)Ph\}\right] \quad (4\text{-}14)$$

$$[W(CO)_5\{C(OMe)Ph\}] + HAuCl_4 \longrightarrow [AuCl\{C(OMe)Ph\}] + WCl_2(CO) \quad (4\text{-}15)$$

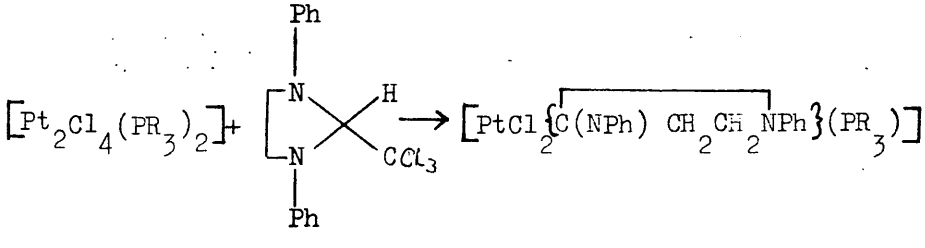
suitable precursors for Pt carbene complexes although their synthetic usefulness may be low as there are many simpler routes to Pt carbenes.

c) Syntheses from carbene precursors

This group includes organic precursors which by elimination of part of the molecule would lead to carbene ligands which are stabilised by complexation to the metal. (Note, however, that the mechanism does not require the formation of the carbene prior to complexation). Electron rich olefins have been used to prepare carbene complexes of many transition metal complexes, including Pt using bis (cyclicdiamine)olefins[128] or bis(cyclicamine(thio))olefins[129] (eqns. 4-16, 4-17). Another successful precursor has been an

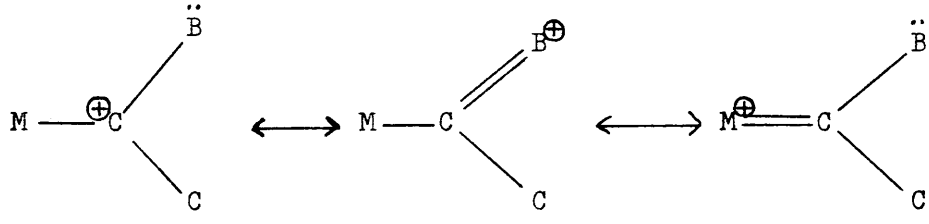


imidazoliline which eliminates chloroform to produce a carbene (eqn. 4-18)[130].



4-3 - Structure and bonding of platinum carbenes

One important fact can be observed from the preceding section, - all platinum carbene complexes so far prepared have either one or two heteroatoms (O, N or S) directly bonded to the carbene carbon and this situation persists in the vast majority of all transition metal carbene complexes. Furthermore, in an sp^2 hybridised carbene carbon, an empty p-orbital will be vacant for π-bonding either with the metal or to the heteroatom. Resonance structure 4-I, 4-II and 4-III add to the stability of metal carbenes (shown for the case of one heteroatom B). 4-I represents σ-donation of the carbene "lone pair" to the metal



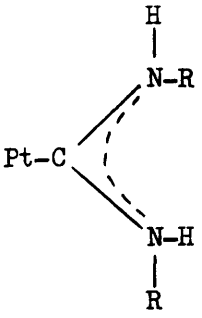
4-I 4-II 4-III

centre, 4-II shows formation of a covalent π-bond of the type found in organic carbonyls and imines and 4-III is metal to ligand back-bonding, analogous to that found in CO and C_2H_4 complexes. This multiple bonding forces the M-C(B)C unit into a planar configuration.

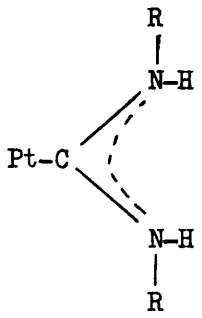
The crystal structures for many Pt(II) carbenes have been determined[131]. Typically the Pt-C bond is 2.0-2.1Å. It has been calculated that the sum of the covalent radii of Pt(II) (1.31Å) and an sp^2 hybridised carbon (0.73Å) is 2.04Å[132]. The similarity of observed values with this, calculated for a purely σ-Pt-C bond, indicates that there is little π-back bonding from the metal to the ligand. There is considerable variation in the Pt-C bond length when the trans ligand is changed due to differing trans influences. So, shorter Pt-C bonds are found when Cl is trans to the carbene ligand

compared with Me or R_3P trans to carbene. The Pt-C bond length should be compared to those found in Pt carbonyls (Pt-C ~1.75Å) and Pt isocyanides (Pt-C ~1.9Å), both of which are considerably shorter than the sum of covalent radii of Pt(II) and C(sp^3) (2.01Å) indicating a high degree of π-back bonding and multiple bond character in the Pt-C bond for these two ligands. Nmr spectroscopy show that there is hindered rotation about the Pt-C bond[133] but this is due to steric hinderance rather than any double bond character in the metal-carbene bond[134]. In the solid state the plane of the carbene ligand is nearly perpendicular to the plane of the platinum-ligand framework and unfavourable steric interactions prevent rotation of the carbene through the plane of the platinum ligands. (In Chugaev's salt[114] and $[\overline{Pt(dppe)\{C(NHtol)=NH[o\text{-}C_6H_4(Me\text{-}p)]\}}]$[135] where the carbene is part of a chelating ligand, the carbene and platinum units are cc-planar).

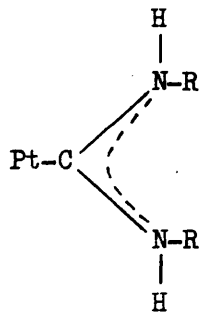
Analysis of the available crystal structure data[131] also shows how important resonance form 4-II is in stabilising the electron deficient carbene. For ligands containing the unit Pt-C(N)X (X = O, N or S) C-N bond lengths are typically 1.31-1.33Å, considerably shorter than a C-N single bond (by the sum of covalent radii = 1.51Å) although longer than the C=N bond in a free imine (e.g. RN=CHCHC=NR, C=N = 1.26Å[136]). Carbene carbon to oxygen bonds are similarly shortened (1.2-1.3Å) compared with C-O single bonds (1.51Å). This high degree of double bond character manifests itself in hindered rotation about the C-N or C-O bond. Nmr studies in $[Pt\{C(NHMe)_2\}_4]^{2+}$[115] and $[PtL_n\{C(NHPh)_2\}]$[132] showed that the carbene adopted the amphi configuration (4-IV) with some trans, trans (4-V) also present but no cis, cis (4-VI) detectable. The tetracarbene dication showed no sign of rotation or isomerisation about the C-N bond even at 90°C[133], indicating a considerable degree of double bond character in this bond.



4-IV



4-V

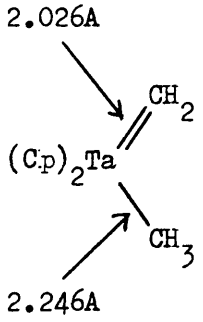


4-VI

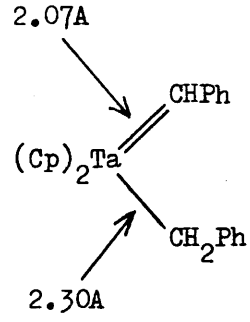
The importance of the heteroatom in stabilising the carbene complexes can be clearly seen when compared with carbenes without a stabilising heteroatom. These are often called Schrock type carbenes after R.R. Schrock who first prepared a tantalum carbene in 1974[137] (eqn. 4-19). In these complexes resonance form 4-II cannot contribute

$$[TaCl_2(CH_2CMe_3)_3] + 2LiCH_2CMe_3 \longrightarrow [Ta(CH_2CMe_3)_3\{C(CMe_3)H\}] + 2LiCl+CMe_4 \qquad (4\text{-}19)$$

to the bonding scheme and there is good evidence that metal to ligand back bonding is important. This is reflected in shorter metal-carbon bonds between metal and carbene than metal and alkyl, as shown in 4-VII[138] and 4-VIII[139], and proton nmr shows hindered rotation of the methylene



4-VII



4-VIII

group in 4-VII which is unlikely to be due to steric hinderance in this case. These complexes are highly sensitive to oxygen and water and decompose at lower temperatures than complexes containing heteroatom stabilised carbenes. So 4-VII decomposes at room temperature whilst

Schrock's original complex decomposes at 71°C, whereas for comparison the neutral amino(organo)-carbene platinum(II) complexes are stable even at over 200°C (see Table 4-3).

4-4 - Chemical properties of Pt(II) carbenes

Compared with the carbene complexes of chromium, molybdenum and turgston, platinum(II) carbene complexes are very much less reactive. However, certain interesting reactions can occur. Some of these have already been dealt with in section 4-2 where the conversion of Pt(II) carbene complexes to new Pt(II) or Pt(IV) complexes was discussed (eqns. 4-10, 4-11, 4-12, 4-13). Deprotonation of the nitrogen heteroatom in carbon ligands has also been mentioned (eqn. 4-9). De-protonation can also occur at the carbon atom directly attached to the carbene carbon (i.e. the α-carbon)[57] (eqn. 4-20, X=Cl,CF_3, L=PMe_2Ph,$AsMe_3$, R=H,Me, ps = proton sponge 1,8-bis(dimethylamino)napthalene). The deprotonation of carbene complexes will be returned to later in the chapter (see

$$\underline{trans}\text{-}[PtX\{C(OMe)CH_2R\}L_2]^+ + ps \longrightarrow \underline{trans}\text{-}[PtX\{C(OMe)=CHR\}L_2] + psH^+ \qquad (4\text{-}20)$$

section 4-6.4). Platinum carbene complexes can also react with phosphine and halides, but again this will be discussed more fully later.

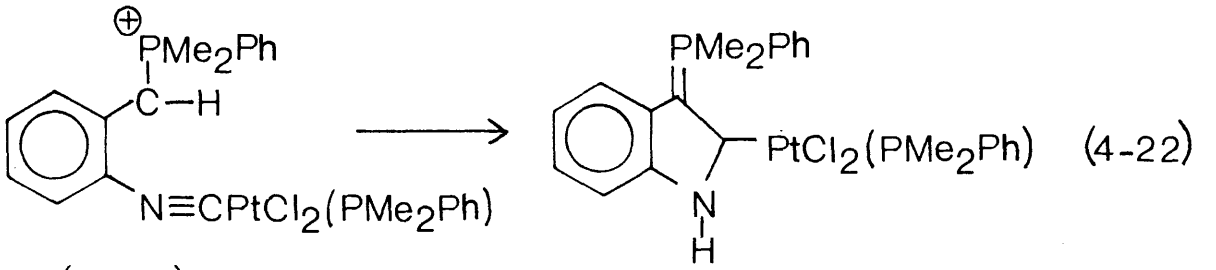
It has been mentioned above that both neutral and cationic platinum alkoxy(organo)carbene complexes - that is complexes containing the unit $Pt\text{-}C(OR)R^1$ - have been prepared and investigated[57,120,121,123] and also that cationic amino(organo)carbene complexes of platinum have similarly been the subject of investigation[125]. There have been previously only two reports of neutral amino(organo)carbene platinum complexes, one prepared by re-arrangement of a platinacycle[140] (eqn. 4-21), the other by the cyclisation of an activated isocyanide type

type complex[141] (eqn. 4-22). In this chapter the synthesis of neutral

$$Pt(PPh_3)_3 + 2(Me_2N{=}CH_2)Cl \longrightarrow [\overline{PtCl\{N(Me)_2CH_2N(Me_2)CH_2\}(PPh_3)}]^+ + Cl^- + 2PPh_3 \quad (4\text{-}21)$$

$$\downarrow$$

$$\underline{cis}\text{-}[PtCl_2\{C(NMe_2)H\}(PPh_3)] + Me_3N$$



(4-22)

amino(organo)carbene platinum complexes is discussed and their low chemical reactivity described. A series of amine complexes, trans-$[PtCl_2(NR_3)(PMe_2Ph)]$, prepared as intermediates in the carbene synthesis is also described.

4-5 - Platinum imine complexes

Organic compounds of the type $R_2C{=}NR$, that is, compounds containing the imine functional group, contain a lone pair of electrons on the nitrogen atom, in exactly the same fashion as amines R_3N. It would be expected then that this type of compound would ligate platinum (and other metal centres) in a manner analogous to amines. This is borne out in practice, for example the action of amines[142] and imines[143] on halide bridged platinum dimers is very similar, yielding σ-N bonded complexes (eqns. 4-23,4-24). This represents the usual method of preparing imine

$$[Pt_2Cl_4(PEt_3)_2] + 2Et_2NH \longrightarrow \underline{trans}\text{-}[PtCl_2(NHEt_2)(PEt_3)] \quad (4\text{-}23)$$

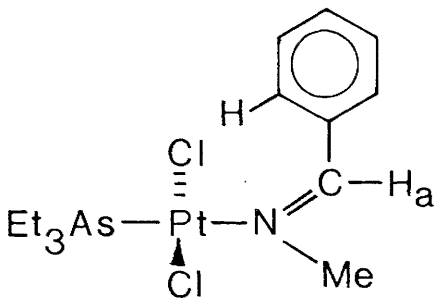
$$[Pt_2Cl_4(AsMe_3)_2] + 2PhNCHPh \longrightarrow \underline{trans}\text{-}[PtCl_2\{N(Ph)CHPh\}(AsMe_3)] \quad (4\text{-}24)$$

complexes, with prior synthesis of the imine followed by nucleophilic attack by the imine at Pt. Imines have also been made by alcohol addition across a nitrile triple bond[144] (eqn. 4-25). Here there is

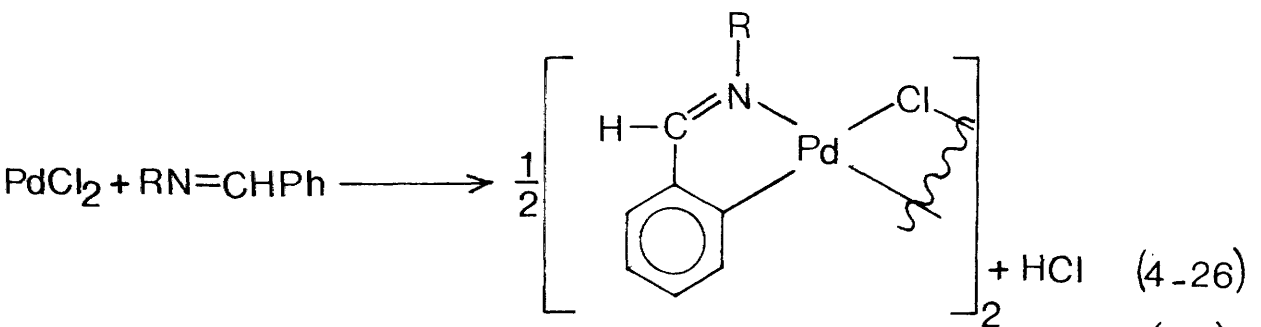
$$\underline{\text{trans}}\text{-}[PtCl(Me)L_2] + N{\equiv}C.C_6F_4.CN \xrightarrow[Ag^+]{EtOH} \underline{\text{trans}}\text{-}[PtMeL_2\{N(H){=}C(OEt).C_6F_4.CN\}]^+ \quad (4.25)$$

an obvious similarity to alcohol addition across isonitriles to give carbenes (eqn. 4-3). Confirmation of a σ-N bonding ligand was provided by the crystal structure determination of $\underline{\text{trans}}\text{-}[PtCl_2\{N(Me)CH(\underline{\text{tol-p}})\}(AsEt_3)]$[145] which showed the ligand to adopt the conformation shown in 4-IX with the proton attached to the imine double bond (which shall be

4-IX



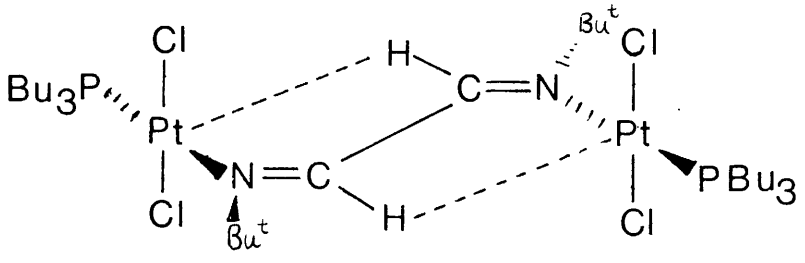
referred to as the imine proton, H_A in 4-IX) trans to Pt and a close, non-bonding approach (2.4Å) between an ortho proton in the tolyl group and the metal atom. This close approach between the metal centre and the ortho proton is thought to be important in ortho metallation reactions of the type found between Pd and imine ligands (eqn. 4-26)[146].



Similar ortho metallations are found in the reactions of imines with Ir[147] and azobenzene with Pd[148].

A large amount of research has been performed by van Koten and co-workers on the conjugated di-imine system (RN=C(R)-C(R)=NR), where the ligand may be either chelating, bridging two metal centres or mono-dentate[136,147]. In addition the π-electrons can be used to form π-bonds to metals,

although no examples of this are known for platinum. It has been found that for mon-dentate or bridging di-imines there is a close approach between the β-hydrogen and the metal centre[148] (e.g. in trans-$[\{PtCl_2(PBu_3)\}_2\{Bu\text{-}N{=}CH.CH{-}NBu^t\}](4\text{-}X)$ $|Pt\text{-}H\beta|$=2.6A. This also forces the imine proton into a configuration trans to the Pt centre.



4-X

There appears to be, on paper at least, a close similarity to the imines and the aminocarbenes. De-protonation of the imine proton or the N-H proton of the carbene could lead to a very similar set of complexes (fig. 4-1), as well as products which could possibly undergo reversible isocyanide deinsertion. The attack of $HgPh_2$ on co-ordinated phenylisocyanide led to the formation of an aminocarbene[150], the reverse of the reaction shown in fig. 4-1. The attempted deprotonations of both types of complex are discussed in this chapter.

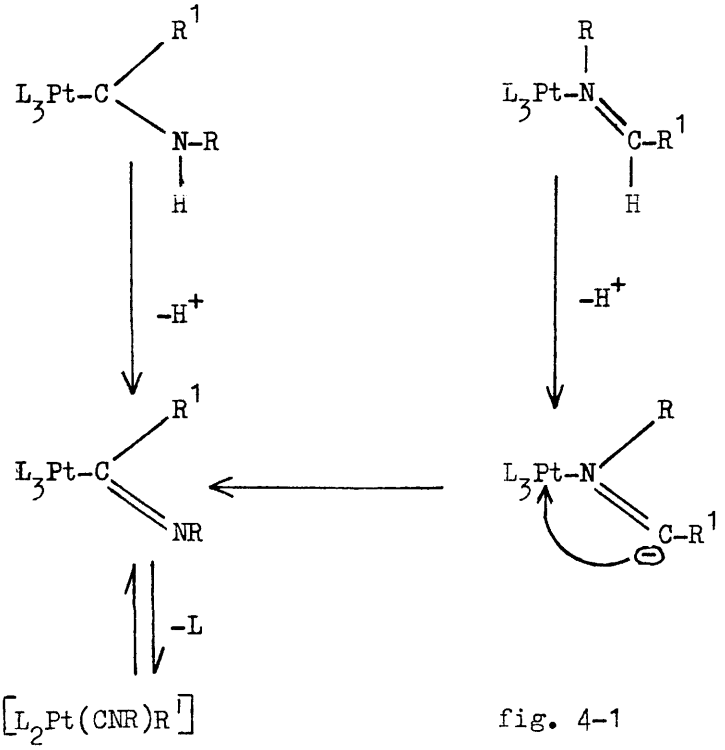


fig. 4-1

4-6 - Results and Discussion

4-6.1 - Platinum amine complexes

Anderson and Cross[121] succeeded in isolating alkoxy(organo) carbene complexes by adding excess alcohol, and phenylacetylene to chloroform solutions of $[Pt_2X_4L_2]$ (X = Cl, Br,I; L = PMe_2Ph,PEt_3) and stirring the mixture for 8 hours at room temperature. When the same procedure was followed using aniline instead of ethanol, and increasing the reaction time to 24 hours, removal of solvent from the reaction vessel left a brown oil which smelt strongly of aniline, due to the excess of that reagent present. The crude product was re-crystallised from CH_2Cl_2/light petroleum to afford yellow crystals. Microanalysis showed that the product was most likely $[PtCl_2(NH_2Ph)(PMe_2Ph)]$ (see Table 4-1). This was confirmed by ^1H nmr spectroscopy which contained signals for the aromatic protons and the phosphine methyl group (intensity 9:6) as well as a broad signal at δ5.2 (intensity 2) assigned to the protons directly attached to nitrogen. Many complexes of the type <u>trans</u>-$[PtX_2(NR_3)(PR_3)]$ have been prepared previously[142,151] by treating halide bridged dimers with an amine (eqn. 4-27). The equilibrium lies to the right when X = Cl or Br, although to the left for X = I. The product geometry is invariably

$$[Pt_2X_4(PR_3)_2] + 2am \rightleftharpoons 2\ \underline{trans}\text{-}[PtX_2(am)(PR_3)] \quad (4\text{-}27)$$

<u>trans</u> and this was also found to be the case for the new aniline complex, whose ir spectrum contained only one (Pt-Cl) stretch (328cm^{-1}), whereas a <u>cis</u> complex would be expected to show two such stretching modes, due to both a symmetric and an asymmetric bending mode. The ^{31}P nmr spectrum contained no signals for the starting dimer indicating that equilibrium (4-27) lies well to the right in this case. The

Table 4-1 Physical data for trans-$[PtCl_2(am)(PMe_2Ph)]$

am	M.Pt (°C)	%C	%H	%N
NH_2Bu^t	137-138	30.43(30.20)	4.75(4.65)	2.92(2.93)
NH_2Me	125-131(dec)	24.81(24.84)	3.46(3.71)	3.22(3.22)
$NHEt_2$	90-91	30.10(30.19)	4.69(4.65)	2.93(2.93)
NH_2Ph	182-184	33.84(33.82)	3.38(3.65)	2.78(2.82)
$NH_2C_6H_4OMe$-m	162-164	34.00(34.17)	3.92(3.82)	2.34(2.66)
$NH_2C_6H_4NO_2$-p	183-185	31.10(31.01)	3.21(3.16)	4.93(4.17)
$NHPh_2$	125-126	41.57(41.90)	3.72(3.87)	2.13(2.44)

Theoretical values shown in parenthesis.

Table 4-2 Spectroscopic Parameters for trans-$[PtCl_2(am)(PMe_2Ph)]$

am	pKa (a)	^{31}P(b) δ_P	$^1J_{PtP}$	^1H δ_{MeP}	$^2J_{HP}$	$^3J_{HPt}$	Others	ir $\nu_{(Pt-Cl)}$	ir $\nu_{(N-H)}cm^{-1}$
NEt_3	11.01	-22.0	3417	1.75	12	29	δ_{CH_2} 3.10(q) δ_{CH_3} 1.25(t)		
NH_2Bu^t	10.83	-24.0	3474	1.78	11	30	δ_{Bu^t} 1.4 δ_{NH} 3.2(br)	337	3210, 3245
NH_2Me	10.66	-23.8	3431	1.78	11	30	δ_{MeN} 2.6 J_{HP} 4.0 J_{HPt} 12.0	328	3145, 3220, 3245, 3280.
$NHEt_2$	10.49	-23.2	3424	1.75	11	29		342	3230
NH_2Ph	4.63	-23.1	3673	1.76	12	32	δ_{NH} 5.2(br)	338	3285, 3105.
$NH_2C_6H_4OMe$-m	4.23	-23.1	3616	1.62	12	33	δ_{OMe} 3.68; δ_{NH} 5.0(br)	345	3220, 3260
$NH_2C_6H_4NO_2$-p	1.00	-22.3	3666	1.80	12	33	δ_{NH} 5.5(br)	343	3205, 3240.
$NHPh_2$	0.79	-22.2	3709	1.72	12	36	δ_{NH} 4.0(br)	340	3190

(a) Values from Handbook of Chemistry and Physics, 67th ed. (1986-1987) CRC PRESS.

(b) Chemical shifts in ppm. chemical coupling constants in Hz.

magnitude of the phosphorus platinum coupling constant is dependent upon the ligand *trans* to the phosphine in the complex and so is normally very useful in assigning the geometry of the complex. In this case the similar low *trans* influence of amine and chloride[152] made the assignment by this parameter impossible (e.g. *trans*-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$, (P *trans* to N), $[PtCl_3(PMe_2Ph)]^+$ (P *trans* to Cl), and *cis*-$[PtCl_2(PMe_2Ph)_2]$ (P *trans* to Cl) have $^1J_{PPt}$ 3673, 3745 and 3546 Hz respectively). It should be noted that even though a large excess of amine was used, no bis(amine) complex was isolated, so equilibrium (4-28) must lie well to the left (or be very slow in forming), also excess amine did not catalyse a *trans* to *cis* isomerisation of the monoamine product.

$$\textit{trans}\text{-}[PtCl_2(NH_2Ph)(PMe_2Ph)] + NH_2Ph \rightleftharpoons [PtCl(NH_2Ph)_2(PMe_2Ph)]^+ + Cl^- \qquad (4\text{-}28)$$

In a similar experiment with $[Pt_2Cl_4(PMe_2Ph)_2]$ and excess phenylacetylene with just one equivalent of *para*-nitroaniline again no carbene complex was formed after being allowed to react for 24 hours and yellow crystals were isolated after solvent reduction and addition of light petroleum. Physical and spectroscopic data (Tables 4-1, 4-2) showed that the amine complex, *trans*-$[PtCl_2(NH_2.C_6H_4.NO_2\text{-}p)(PMe_2Ph)]$, was the only product.

Trans-$[PtCl_2(NH_2C_6H_4OMe\text{-}m)(PMe_2Ph)]$ was similarly prepared as yellow crystals by simple bridge cleavage and the same technique was used to prepare the other amine complexes listed in Table 4-1, although the problems that were encountered in the synthesis of some of the complexes are described in more detail below.

Addition of diethylamine to a $CHCl_3$ solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ caused an immediate colour change in solution from orange to yellow (a similar fast colour change was observed in all amine bridge-cleavage

reactions.) However, after solvent removal and re-crystallisation of the crude product from CH_2Cl_2/MeOH, colourless crystals of cis-$[PtCl_2(PMe_2Ph)_2]$ were isolated (confirmed by comparison of its ir and nmr spectra with authentic samples). The proton nmr of the remaining dissolved material was complicated, probably due to there being a mixture of products present. The crude product was re-dissolved in benzene and all the remaining cis-$[PtCl_2(PMe_2Ph)_2]$ was removed by filtration. The benzene solution was chromatographed through a silica gel column which caused elution of a yellow solution whilst a dark brown material bound irreversibly to the gel at the top of the column. The soluble fraction was dried and re-crystallised from ether/pentane to produce yellow crystals of trans-$[PtCl_2(NHEt_2)(PMe_2Ph)]$ (Table 4-1). Ir and nmr spectroscopy confirmed this assignment (Table 4-2) although the proton nmr was complicated with the ethyl groups appearing to be inequivalent. It seems likely that the brown material was $[PtCl_2(NHEt_2)_2]$ which decomposed in the chromatography column.

A $CDCl_3$ solution of trans-$[PtCl_2(NHEt_2)(PMe_2Ph)]$ remained unchanged over 24 hours, so the bis(phosphine)species cannot have been produced by the disproportionation reaction (eqn. 4-29).

$$2\ \text{trans-}[PtCl_2(NHEt_2)(PMe_2Ph)] \rightleftharpoons \text{cis-}[PtCl_2(PMe_2Ph)_2] + [PtCl_2(NH_2Et)_2] \qquad (4\text{-}29)$$

The mechanism must involve the breaking of Pt-P bonds. This could be caused by poor mixing of the amine resulting in small volumes of the reaction vessel containing higher concentrations of diethylamine. This could cause either the amine replacement of a phosphine (eqn. 4-30) or the formation of a bis(amine)phosphine complex which then undergoes phosphine elimination (eqn. 4-31). The free phosphine could then react with either the amine phosphine complex (eqn. 4-32) or unreacted dimer.

(eqn.4-33) to produce the bis(phosphine) complex. The operation of (4-31) seems more likely than (4-30) as such bis(amine)phosphine

$$\underline{\text{trans}}\text{-}[PtCl_2(NHEt_2)(PMe_2Ph)] + NHEt_2 \rightleftharpoons [PtCl_2(NHEt_2)_2] + (PMe_2Ph) \quad (4\text{-}30)$$

$$\Downarrow\Uparrow$$

$$[PtCl(NH_2Et)_2(PMe_2Ph)]^+ + Cl^- \rightleftharpoons [PtCl_2(NHEt_2)_2] + PMe_2Ph \quad (4\text{-}31)$$

$$\underline{\text{trans}}\text{-}[PtCl_2(NHEt_2)(PMe_2Ph)] + PMe_2Ph \longrightarrow \underline{\text{cis}}\text{-}[PtCl_2(PMe_2Ph)_2] \quad (4\text{-}32)$$

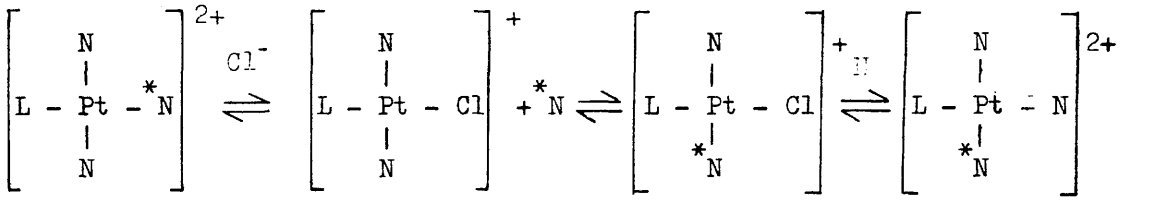
$$\tfrac{1}{2}[Pt_2Cl_4(PMe_2Ph)_2] + PMe_2Ph \longrightarrow \underline{\text{cis}}\text{-}[PtCl_2(PMe_2Ph)_2] \quad (4\text{-}33)$$

complexes of platinum have been isolated (see below) whilst (4-30) involves replacement of a phosphine trans to a group of low trans-effect.

Similar problems were encountered in the preparation of trans $[PtCl_2(NH_2Bu^t)(PMe_2Ph)]$. Again cis-$[PtCl_2(PMe_2Ph)_2]$ was isolated in significant ($\sim$30%) quantities. Pure product was obtained by passing a benzene solution of the crude product through a chromatography column containing silica gel, which again eluted a yellow solution with a dark brown material remaining in the column. The yellow solution was dried and re-crystallised from CH_2Cl_2/MeOH. No further reaction took place on re-crystallisation indicating that it was not the original addition of methanol to the crude product which produced cis-$[PtCl_2(PMe_2Ph)_2]$. Physical and spectroscopic data for the complex are presented on Tables 4-1 and 4-2.

Initial attempts to prepare trans-$[PtCl_2(NH_2Me)(PMe_2Ph)]$ were also unsuccessful, although for a different reason. When methylamine gas was passed through a chloroform solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ there was the usual orange to yellow rapid colour change indicating the formation of trans-$[PtCl_2(NH_2Me)(PMe_2Ph)]$. After 10 minutes the gas flow was halted and the flask stoppered with the solution being stirred. After

30 minutes the yellow colour had gone, leaving a colourless solution. On stirring for a further 24 hours, a white precipitate formed which was removed by filtration. The compound was soluble in CD_3OD and the proton nmr showed signals for the phosphine methyls (δ1.97ppm, J_{HPt} 39, J_{HP} 11Hz, intensity=6) and the amine methyl group (δ 2.35ppm, J_{HPt} 43Hz intensity = 9) implying the empirical formula $[Pt(NH_2Me)_3(PMe_2Ph)]Cl_2$. There was only one signal for MeN in the proton nmr spectrum although it was slightly broadened, either due to chance overlap of the two types of amine methyl groups, or else due to rapid amine exchange (eqn. 4-34, L = PMe_2Ph, N = NH_2Me).



(4-34)

The latter pathways seem most likely as the solution tended to lose NH_2Me. Refluxing in MeOH for 30 minutes led to the formation of a new species, both methanol and chloroform soluble whose physical and spectroscopic parameters fitted the formulation <u>trans</u>-$[PtCl(NH_2Me)_2(PMe_2Ph)]Cl$. The geometry was assigned from the ir and proton nmr spectra of this complex. The former contained one Pt-Cl stretch (283cm^{-1}) and many N-H stretches (>3000cm^{-1}). The Pt-Cl stretch is typical of a Cl <u>trans</u> to a phosphine, <u>cis</u> complexes with Cl <u>trans</u> to an amine would be expected to have ν(Pt-Cl) $\sim$340cm^{-1}, i.e. the same region as Cl <u>trans</u> to Cl. In the proton nmr spectrum in $CD_3OD/CDCl_3$ (1:1) the methylnitrogen groups were equivalent (δ_{MeN} 2.35, J_{PtH} 12, J_{PH} = 0Hz). The equivalence of the two groups and the lack of coupling to phosphorous in <u>trans</u>-$[PtCl_2(NH_2Me)(PMe_2Ph)]$ ($J_{\underline{MeNPtP}}$ = 4Hz) indicate that the

methylamine ligands are trans to each other and cis to the phosphine. The complex geometry would be expected to be trans as the amine trans to the phosphine (the ligand of highest trans effect) is the ligand most likely to be replaced. Refluxing the bis(amine)phosphine complex in ethanol for 6 hours did not lead to further loss of methylamine, so the monoamine complex could not be synthesised via this route.

In separate reaction $[Pt_2Cl_4(PMe_2Ph)_2]$ reacted with $MeNH_2$ gas to produce only the bis(amine) complex in the trans configuration. Since it seems likely that trans-$[PtCl_2(NH_2Me)(PMe_2Ph)]$ would react with methylamine to produce cis-$[PtCl(NH_2Me)_2(PMe_2Ph)]^+$ initially, isomerisation to the trans form must have taken place prior to isolation of the amine complex, probably via the tris(amine) complex and amine loss.

The desired compound was finally synthesised by using a solution of $MeNH_2$ in industrial spirit. In this way the stoichiometry of the reaction could be controlled and yellow crystals of trans-$[PtCl_2(NH_2Me)(PMe_2Ph)]$ were easily obtained in high yield. When 4 equivalents of Me_2NH were added to a solution of the starting dimer only the mono(amine) complex was formed, indicating that equilibrium (4-35) lies well to the left and high concentrations of methylamine are required to form the

$$\text{trans-}[PtCl_2(NH_2Me)(PMe_2Ph)] + NH_2Me \rightleftharpoons [PtCl(NH_2Me)_2(PMe_2Ph)]Cl \quad (4\text{-}35)$$

bis and tris(amine) species, a condition that would be encountered when saturated chloroform solutions of the amine were used.

The diphenylamine complex trans-$[PtCl_2(NHPh_2)(PMe_2Ph)]$ could also be prepared by the standard method if an excess of $NHPh_2$ was used. When pure samples of the product were re-dissolved in $CDCl_3$, ^{31}P nmr. spectroscopy showed that considerable re-dimerisation had taken place, with $[Pt_2Cl_4(PMe_2Ph)_2]$ and amine complex present in nearly equimolar

amounts. It has been previously reported that similar bridge cleavage reactions are in reality equilibria[142], and difficulty in isolating complexes with weakly basic amines were encountered. For instance, attempts to prepare trans-$[PtCl_2(NHPh_2)(PPr^n_3)]$ failed with only isolation of the less soluble starting dimer being possible, even though the desired product was detected in solution. In the present study only diphenylamine complexes showed any sign of re-dimerisation in solution (within the detection limits of ^{31}P nmr spectroscopy).

One other observation can be made from Table 4-2. As the ligands become less basic (i.e. as their pKa values decrease), $^1J_{PtP}$ increases. (NH_2Bu^t and NH_2Ph are exceptions to this rule, but the basicity of the amines in $CDCl_3$ may follow a slightly different order to their basicity in H_2O, the latter being the solvent in which pKa values were determined). This indicates that the trans influence of the amines decreases going to weaker bases. So the more basic amine must be stronger σ-donors (as would be expected due to their electron releasing substituents) and have higher σ-trans influence, which since π-bonding is not important in Pt-N(sp^3) bonds, must equal the total trans influence.

4-6-2 - Synthesis of Pt(II) amino(organo)carbenes

As mentioned in the previous section, attempts to prepare neutral aminocarbene platinum complexes by a method analogous to that used to prepare alkoxycarbene platinum complexes[121] led to amine complex formation. However, by increasing the reaction time to 7 days $[Pt_2Cl_4(PMe_2Ph)_2]$, $PhNH_2$ and $HC{\equiv}CPh$ did react to form a white precipitate in low yield ($\sim$30%.) This solid was insoluble in $CHCl_3$, CH_2Cl_2, C_6H_6 and $(CH_3)_2CO$ but very slightly soluble in MeOH from which it was re-crystallised. From its physical appearance it was not the amine complex

and elemental analysis (Table 4-3) was consistent with the formation of the desired carbene complex $[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$. The presence of two Pt-Cl stretches in the ir spectrum of the complex (280 and 305cm^{-1}) showed that the cis isomer had been formed (All the neutral alkoxycarbene complexes were also cis). Analysis of the mother liquors showed that some trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ and cis-$[PtCl_2(PMe_2Ph)_2]$ were present, along with unidentified organic material. The occurrence of the cis-bis(phosphine) complex is indicative of some decomposition reactions or competing side reactions which had occurred during synthesis.

The mechanism of formation was likely to be very similar to that found for the neutral alkoxycarbenes (eqn. 4-7) although the initial stages of the reaction must follow a different course. For the alkoxycarbenes the first step of the reaction is the cleavage of the halide bridged dimer by the acetylene forming a π-complex which then undergoes rearrangement to the vinylidene. Attack by the alcohol at this reactive ligand then produces the carbene. In the present system the first step must be the rapid cleavage of the halide bridge to form trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ as shown in section 4-6.1. Indeed, if this complex was treated with HC≡CPh, carbene formation proceeded with equal efficiency to starting from the dimer. Two pathways are then possible. Since the amine complex was in equilibrium with the dimer, phenylacetylene could compete in the bridge cleavage reaction, giving a π-complex (eqn. 4-36) which can then react as described already. Alternatively, the phenylacetylene could co-ordinate to the amine complex (with or without the loss of another ligand from the complex)

$$\text{trans-}[PtCl_2(NH_2Ph)(PMe_2Ph)] \underset{NH_2Ph}{\rightleftharpoons} [Pt_2Cl_4(PMe_2Ph)_2] \underset{HC\equiv CPh}{\rightleftharpoons} [PtCl_2(PMe_2Ph)(PhC\equiv CH)] \quad (4\text{-}36)$$

Table 4-3 Physical Data for cis- $[PtX_2\{C(NRR^1)CH_2Ph\}L]$

L	X	R,R^1	M.Pt(^oC)	%C (a)	%H	%N	Others
PMe_2Ph	Cl	H,Ph	243-245	44.24(44.08)	3.63(3.58)	1.87(2.34)	Cl.12.09(11.83); P5.56(5.17)
		H,$C_6H_4NO_2$-p	227-229	41.00(41.01)	3.61(3.60)	4.27(4.35)	
		H,C_6H_4OMe-m	231	43.90(43.89)	4.09(4.16)	1.73.(2.23)	
		Ph,Ph	>205(dec)	49.89(49.78)	3.76(4.18)	1.67(1.59)	
	Br	H,Ph	>207(dec)	38.43(38.19)	3.58(3.51)	1.93(2.09)	Br 22.76(23.22)
PBu_3	Cl	H,Ph	209- 212	47.31(47.06)	6.13(6.06)	2.22(2.11)	

(a) Theoretical values in parenthesis

and then undergo re-arrangement to the vinylidene. Either mechanism would give a rate of reaction much slower than for the alkoxycarbene formation, as the first means a very much lower concentration of the dimer available to react with phenylacetylene, whilst in the second the formation of a complex between the phenylacetylene and the amine complex could be an unfavourable process.

By changing the amine, but using the synthetic route described above, the carbene complexes cis-$[PtCl_2\{C(NH.C_6H_4.NO_2\text{-}p)CH_2Ph\}(PMe_2Ph)]$, cis-$[PtCl_2\{C(NHC_6H_4OMe\text{-}m)CH_2Ph\}(PMe_2Ph)]$ and cis-$[PtCl_2\{C(NPh_2)CH_2Ph\}(PMe_2Ph)]$ were synthesised. The latter proved difficult to purify, requiring three successive re-crystallisations from $CHCl_3$/light petroleum before an analytically pure sample of the complex was obtained. Starting from $[Pt_2Br_4(PMe_2Ph)_2]$, phenylacetylene and aniline the highly insoluble bromo complex cis-$[PtBr_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ was isolated although due to its low solubility, further purification proved impossible. When the phosphine was changed to tributylphosphine the chloroform soluble complex cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ was isolated from the reaction between $[Pt_2Cl_4(PBu_3)_2]$, $HC{\equiv}CPh$ and NH_2Ph. The physical and infra red data for all the carbene complexes successfully synthesised are shown in Tables 4-3 and 4-4.

Not all the amine complexes could be converted to aminocarbene complexes, however. With the more basic amines, Et_2NH, Bu^tNH_2 and $MeNH_2$ only brown waxy solids were formed which gave complicated ir and nmr spectra, none of which contained any evidence for the formation of carbene products. No, or very little, starting material was detected, so either unfavourable side reactions prevented the formation of the carbene or else carbenes were formed but then underwent further decomposition. Decomposition of cationic aminocarbenes have been previously observed[125] in the aminolysis of cationic alkoxycarbene

Table 4-4 Infrared Data for Pt-Aminocarbenes

	ν(Pt-Cl)(cm^{-1})	ν(N-H)(cm^{-1})
cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$	280,305	3130,3170
cis-$[PtCl_2\{C(NHC_6H_4NO_2\text{-}p)(CH_2Ph)\}(PMe_2Ph)]$	280,305	3145
cis-$[PtCl_2\{C(NHC_6H_4OMe\text{-}m)CH_2Ph\}(PMe_2Ph)]$	280,305	3130,3180
cis-$[PtCl_2\{C(NPh_2)CH_2Ph\}(PMe_2Ph)]$	283,307	—
cis-$[PtBr_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$	—	
cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$	230,305	3130,3180

complexes. So in the reaction of the alkoxycarbenes with $NHMe_2$, NH_2Me or NH_3, aminocarbene complexes were obtained (eqn. 4-37), whereas in

$$\underline{trans}\text{-}[Pt(CH_3)\{C(OMe)R\}(PMe_2Ph)_2]^+ + NHR^1{}_2 \rightarrow \underline{trans}\text{-}[Pt(CH_3)\{C(NR^1{}_2)R\}(PMe_2Ph)_2]^+ + MeOH \quad (4\text{-}37)$$

the reactions with Et_2NH, Pr_2NH or Bu^tNH_2, although the alkoxycarbene did react, no aminocarbenes could be isolated, and extensive decomposition appeared to take place, and like above, only intractable residues were obtained.

Decomposition products were also obtained when phenylacetylene was replaced with methylacetylene in an attempt to synthesise $\underline{cis}$-$[PtCl_2\{C(NHPh)Et\}(PMe_2Ph)]$. It would seem, therefore, that electron withdrawing groups are required on both α-substituents to stabilise the product.

An attempt to prepare an aminocarbene containing a double bond from nitrogen to the β-carbon also failed. The imine complex $\underline{trans}$-$[PtCl_2(NH{=}CPh_2)(PMe_2Ph)]$ was easily prepared and fully characterised (see section 4-6.5. After being allowed to react with phenylacetylene for 24 hours, ^{31}P nmr spectroscopy showed that many phosphorus containing materials were present, including the starting imine complex ($\sim$10%) and $\underline{cis}$-$[PtCl_2(PMe_2Ph)_2]$ ($\sim$30%) as well as an unidentified species ($\sim$40%) with parameter δ -17.7 J_{PtP} 3800Hz, possibly due to some carbene complex. The only product isolated from the reaction was $\underline{cis}$-$[PtCl_2(PMe_2Ph)_2]$, probably arising from decomposition of the carbene species, none of which was isolated or detected in the final residue.

Aminolysis of alkoxycarbene chromium complexes has been widely used in the formation of aminocarbene chromium complexes[116] and in particular $HN{=}CPh_2$ has been used to prepare a carbene complex[153] (eqn. 4-38) so carbene ligands can be prepared from this amine. The failure

for the platinum complex reflects the fact that more basic amines do

$$[Cr(CO)_5\{C(OMe)(Me)\}] + HN{=}CPh_2 \longrightarrow [Cr(CO)_5\{C(N{=}CPh_2)Me\}] + HOMe \quad (4\text{-}38)$$

not lead to aminocarbene complexes.

Cyclic aminocarbenes could also be prepared by the same synthetic route used to prepare the amino(benzyl)carbene platinum complexes. Ortho-aminophenylacetylene reacted rapidly with a platinum halide bridged dimer to form the cyclic carbene[154] (eqn. 4-39) with the reaction being complete within one hour at room temperature. The

$$\tfrac{1}{2}[Pt_2Cl_4(PBu_3)_2] + HC{\equiv}C.C_6H_4.NH_2\text{-}o \longrightarrow \underline{cis}\,[PtCl_2(C_8H_6N)(PBu_3)] \quad (4\text{-}39)$$

dramatic increase in rate is due to the necessary proximity of the alkynyl group to the (presumed) initial platinum amine complex, increasing the probability of further reaction.

4-6-3 - Nmr spectroscopic properties and stereochemistry of aminocarbene complexes of platinum.

Due to the nature of the phosphine ligand cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ was more soluble in $CDCl_3$, than any of the dimethylphenylphosphine complexes, although cis-$[PtCl_2\{C(NPh_2)CH_2Ph\}(PMe_2Ph)]$ had appreciable solubility in chloroform. It was relatively simple to record the ^1H nmr spectra for these complexes in $CDCl_3$.

The proton nmr spectra (see fig. 4-2) show many features in common with the complexes cis-$[PtCl_2\{C(OR)CH_2Ph\}(PMe_2Ph)]$[121]. The most noticeable feature is the AB quartet in the region δ4-5ppm due to the benzyl methylene protons (i.e. Pt-$\dot{C}$-$\underline{CH_2}$-Ph). The inequivalence of these protons is indicative of hindered rotation about the Pt-C bond (as mentioned in section 4-3). The protons exhibit geminal coupling with a coupling constant ($^2J_{HH}$=14Hz) consistent with protons bonded to a

Fig.4-2 200MHz ^{1}H n.m.r. Spectrum of

Cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$

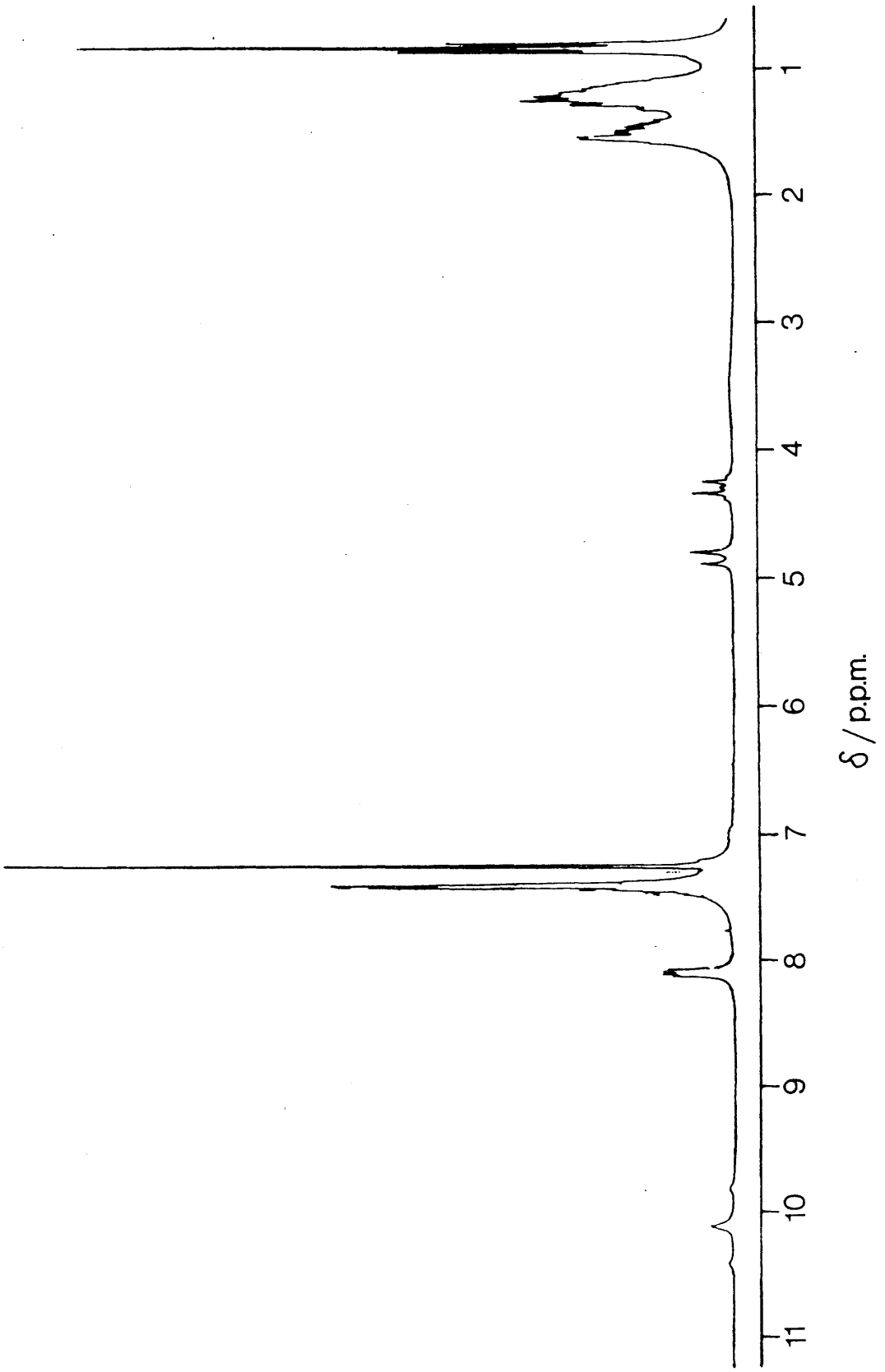
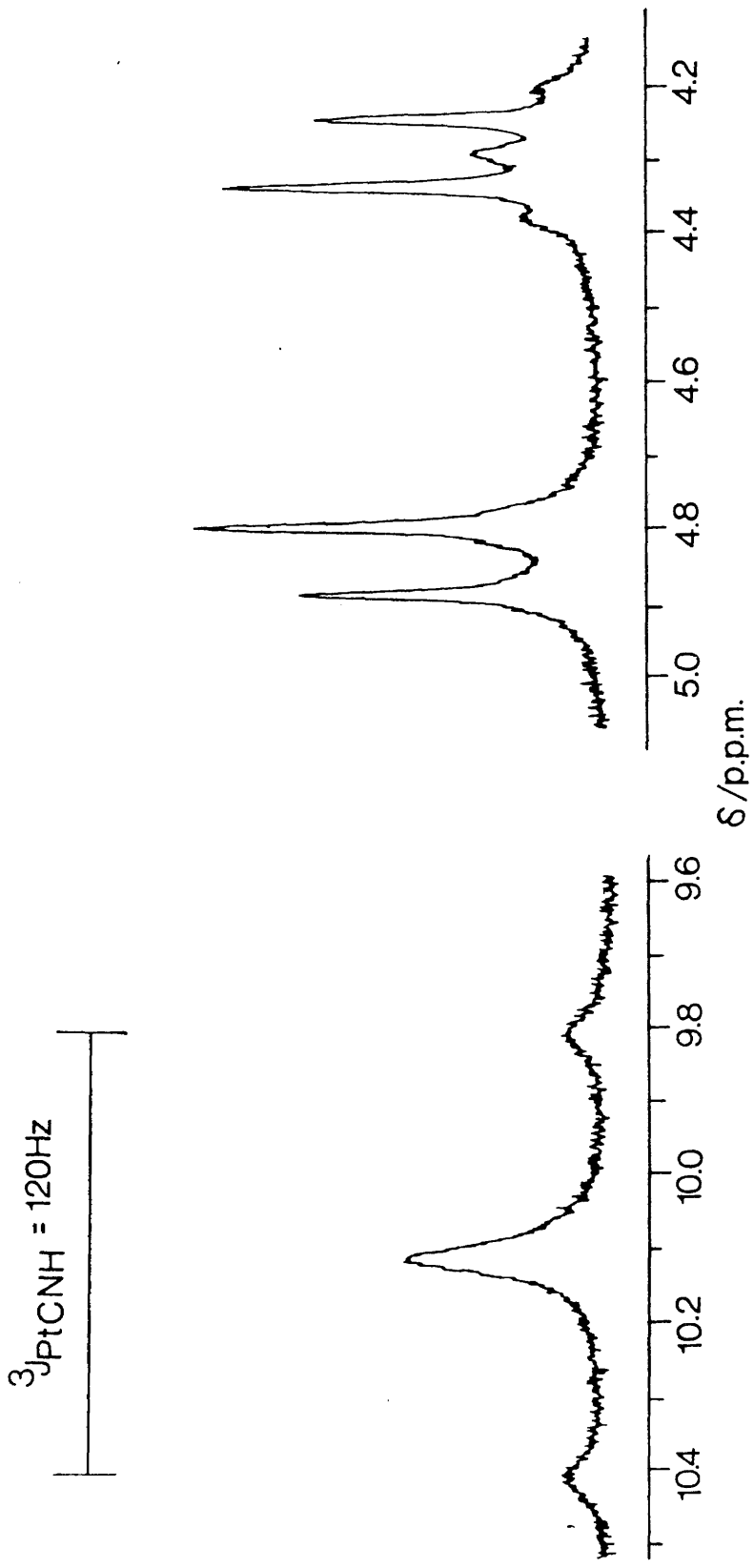


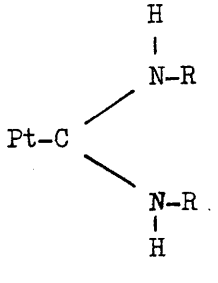
Fig 4-2(b) Expansion of part of Fig 4-2



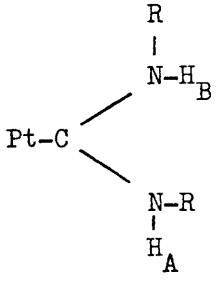
tetrahedral sp^3 carbon atom. Furthermore, one of the methylene protons exhibits coupling to platinum whilst the other does not, again indicative of inequivalent environments, with the former possibly "trans"-like to platinum and the latter "cis"-like.

The phosphine methyls in cis-$[PtCl_2\{C(NPh_2)CH_2Ph\}(PMe_2Ph)]$ also have different magnetic environments (see Table 4-5) although there is overlap of the central signals, the inequivalence being seen in two different magnitudes for $^3J_{PtH}$. This inequivalence is again indicative of hindered rotation about the platinum-carbene carbon bond.

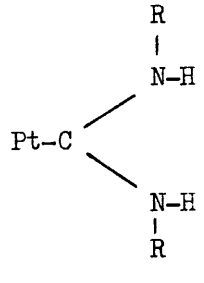
The resonance for the N-H proton is downfield at δ 10.1ppm, indicating a large amount of deshielding. Similar downfield shifts were found in the cationic aminocarbenes[122] and can be explained by noting that due to a resonance contribution of the nitrogen lone pair to the carbene carbon (4-II) the nitrogen atom has a slightly positive charge and the inductive effect of this charge deshields the N-H proton. The proton also couples to platinum ($^3J_{PtH}$=120Hz) and the magnitude of this coupling constant can be used to assign the geometry of the product about the C---N bond. In a study of complexes of the type trans-$[PtX\{C(NHR)_2\}L_2]^+$ (X=Cl,Br; R=Me,Ph; L=PEt_3,PMe_2Ph), Crociani and Richards[155] showed that of the three possible configurations of the carbene ligand (4-XI, 4-XII and 4-XIII) the amphi configuration (4-XII) dominated in solution giving two distinct platinum proton coupling constants of ~30 and ~90Hz which



4-XI



4-XII



4-XIII

Table 4-5 ^{1}H nmr data for aminocarbene complexes.

	solvent	MeP			CH_2Ph			Others	
		δ	$^{2}J_{HP}$	$^{3}J_{HPt}$	δ	$^{2}J_{HH}$	$^{3}J_{PtH}$	δ	$^{2}J_{HPt}$
cis-[$PtCl_2${C(NHPh)CH_2Ph}(PMe_2Ph)]	$CDCl_3$/ CD_3OD	1.25 1.16	11.5 11.6	44.6 46.4	4.55 4.29	14.8	0 37		
cis-[$PtCl_2${C(NPh_2)CH_2Ph}(PMe_2Ph)]	$CDCl_3$	1.28 1.28	11.6 11.6	44.8 48.0	4.57 4.01	14.7	0 47		
cis-[$PtCl_2${C(NHPh)CH_2Ph}(PBu^n_3)]	$CDCl_3$				4.84 4.29	18.2	0 36	δ_{NH} 10.1	$^{2}J_{HPt}$ 120
cis-[$PtCl_2${C(NHC$_6$H$_4$OMe-m)(CH_2Ph)}(PMe_2Ph)]	CD_3OD	1.19 0.99	11.7 11.5	45.7 48.9	4.54 4.25	14	0 44	δ OMe 2.15	
cis-[$PtCl_2${C(NHC$_6$H$_4$NO$_2$-p)(CH_2Ph)}(PMe_2Ph)]^{2}	CD_3OD	1.31 0.95	11.3 11.2	42.0 49.6	4.60 4.31	14	0 44		

could be assigned, by comparison with cyclic carbenes to $^3J_{PtH_A}$ and and $^3J_{PtH(B)}$ respectively. Some trans, trans conformation (4-XIII) was also found in that work ($^3J_{PtH}$ ~90Hz) but no cis, cis ligand due to steric repulsion of the R groups. The coupling constant in the present case (120Hz) quite clearly indicates a trans arrangement around the C---N bond of the platinum and hydrogen nuclei. That the coupling constant is greater than for the diaminocarbenes described above reflects a greater double bond character in the C---N bond for the monoheteroatom carbene than the bis(heteroatom) carbene. This is because the single N atom will contribute more electron density to stabilise the C(sp^2) atom than either of the N atoms in 4-XII, i.e. with two heteroatoms there is competition for overlap with the p_z orbital on the carbene carbon. The effect of this change in C---N bond length depending on the number of α-heteroatoms has been noted previously in crystallographic studies on carbene complexes(156) and is clearly illustrated in Table 4-6, where carbenes with two heteroatoms have |C---N| ~1.33Å whilst much shorter |C---N| distances are found when one heteroatom is present (|C---N| less than 1.3Å).

Addition of a few drops of CD_3OD to a $CDCl_3$ suspension of cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ greatly improved the solubility of the carbene complex. It also caused a considerable change in the proton nmr parameters of the benzyl protons, changing both their chemical shifts (from 4.34 and 4.27ppm to 4.55 and 4.36ppm) and the geminal coupling constant (from 18 to 16Hz). Furthermore, the coupling observed between the platinum and one of the benzyl methylene protons previously observed was removed. The exact reasons for these changes are not clear, but possibly CD_3OD co-ordinates to the platinum centre, or to the carbene carbon. The latter type of co-ordination is important in alkoxy exchange as described in the next section. Either of these co-ordinations would cause a change in the conformation of the

Table 4-6 C-N bond lengths in Pt carbene complexes.

Complex	$\lvert C\!-\!N \rvert$ (Å)
cis-$[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$	1.33
trans-$[PtCl_2\{C(NPh.CH_2)_2\}(PEt_3)]$	1.37/1.33
cis-$[PtCl_2\{C(NPh.CH_2)_2\}(PEt_3)]$	1.33
$[Pt\{C(NHMe)_2\}_4][PF_6]_2$	1.31
trans-$[Pt(CNMe)_2\{C(NHMe)SEt\}_2][PF_6]_2$	1.30
cis-$[Pt(CNMe)_2\ C(NHMe)NMe{=}C(NHMe)][BPH_4]$	1.36
trans-$[PtCl\{C(NMe_2)CH_2CH_2CH_2OH\}(PMe_2Ph)_2][PF_6]$	1.29
trans-$[PtMe\{C(NMe_2)Me\}(PMe_2Ph)][PF_6]$	1.27
cis-$[PtCl_2\{C(NMe_2)H\}(PPh_3)]$	1.25

carbene ligand and a corresponding change in nmr parameters. Similar solvent effects have been noted previously[121,155] where the inequivalence of the phosphine methyl groups could be removed by changing the solvent (although it seems more likely that the groups were still inequivalent but had co-incidental nmr parameters).

The increased solubility of the tributylphosphine complex with CD_3OD addition meant that it became possible to record the ^{13}C nmr spectrum of the complex. This contained the characteristic downfield signal for the electron deficient carbene carbon (δ_C=218ppm) which was a doublet due to coupling to phosphorus ($^2J_{CP}$=5Hz) but the platinum satellites were too weak for an accurate determination of $^1J_{CPt}$. Platinum satellites for the benzyl methylene carbon were observable (δ_C=56.4ppm; $^2J_{CPt}$=60Hz). The values are similar to those found in cationic complexes <u>trans</u>-$[PtCl\{C(NHMe)Me\}(AsEt_3)_2]^+$ (R=H; δ_C=215ppm; R=Me, C=210ppm) $^2J_{PtC}$ 80Hz)[157,158]. The close similarity of the chemical shifts and coupling constants suggests that the extra positive change in the cationic complexes has little effect on the platinum-carbene and intracarbene bonding scheme.

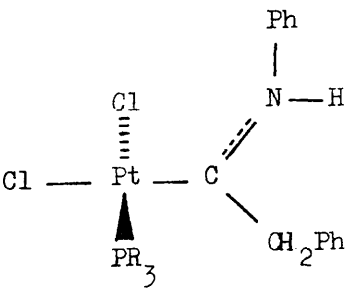
Similar ^1H and ^{13}C chemical shifts were observed for the cyclic carbene <u>cis</u>-$[PtCl_2\{C(NHC_6H_4CH_2\text{-}o)\}(PBu_3)]$[154] with a deshielded carbene carbon (δ_C209 J_{CP} 7Hz) and coupling between the α-carbon and platinum (δ_C54 $^2J_{PtC}$ 90Hz). The amine proton, which must be in a <u>cis</u> arrangement to platinum is typically deshielded, although due to the geometry of the complex it only exhibits a small coupling to platinum (δ_{NH} 13ppm $^3J_{HPt}$ 5Hz).

<u>Cis</u>-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ although insoluble in $CDCl_3$, was soluble in a 1:1 mixture of $CDCl_3/CD_3OD$ and its proton nmr spectrum could be recorded (see Table 4-5). Due to overlap of the residual OH signals from the CD_3OH with the AB quartet of the benzylmethylene protons at

room temperature the spectrum was recorded at +50°C. Most of the features already described were again present. The NH proton signal could not be detected due to H/D exchange with the solvent, but again inequivalent benzyl protons and inequivalent phosphine methyl groups could be observed. It was also observed that neither this complex, nor the tri-butylphosphine analogue showed any sign of decomposition in solution over 24 hours, unlike the neutral alkoxycarbenes which show signs of decomposition (~20%) over a similar time period.

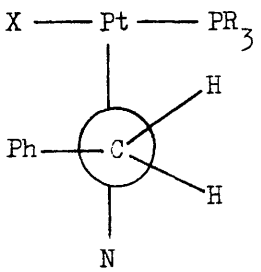
Similarly the complexes cis-$[PtCl_2\{C(NHR)CH_2Ph\}L]$ (R = C_6H_4OMe-m, $C_6H_4NO_2$-p) were highly insoluble in $CDCl_3$ but in CD_3CD their solubility was sufficient to allow the proton nmr parameters to be determined at room temperature (see Table 4-5). Both showed the typical features described above, with an AB quartet for the benzylmethylene protons, with one proton displaying coupling to platinum, and inequivalent methyl groups on the phosphine.

The nmr results, along with crystal structures of other platinum carbene complexes can be used to assign an overall stereochemistry to the aminocarbene. For non chelating carbenes the plane of the carbene is nearly perpendicular to the plane of the platinum ligand framework, and the α-nitrogen atom is trigonal planar due to the re-hybridisation of the lone pair into a $C(p_z)$-$N(p_z)$ double bond. These facts, together with the spectroscopic observation that the halide ions are cis and that the platinum is trans to the amino proton imply an overall stereochemistry shown in 4-XIV. Viewing along the C(carbene)-C bond (4-XV), and placing



4-XIV

the phenyl group in the position of least steric hinderance clearly shows the inequivalence of the benzylmethylene protons, with one proton "trans" like to platinum and the other nearly eclipsed, which explains why only one of these protons exhibited coupling to platinum in the proton nmr spectrum of cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$. Co-ordination of CD_3OD at Pt or the carbene carbon would cause a change in the configuration of the



4-XV

ligand and could easily remove the proton platinum coupling.

4-6.4 - Reactions of amino(organo)carbene complexes of platinum

H/D Exchange Reactions

Deuterated alcohols react with both cationic and neutral platinum alkoxycarbene complexes[57,123] causing both exchange of the alkoxy group (eqn. 4-40) and exchange of the protons on the α-carbon (eqn. 4-41).

$$cis\text{-}[PtCl_2\{C(OMe)CH_2R\}(PMe_2Ph)] + R^1OH \longrightarrow cis\text{-}[PtCl_2\{C(OR^1)CH_2R\}(PMe_2Ph)] + MeOH \qquad (4\text{-}40)$$

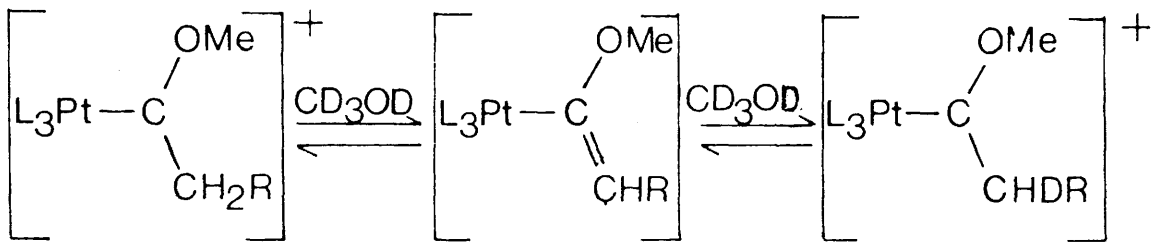
$$cis\text{-}[PtCl_2\{C(OMe)CH_2R\}(PMe_2Ph)] + 2R^1OD \longrightarrow cis\text{-}[PtCl_2\{C(OMe)CD_2R\}(PMe_2Ph)] + 2R^1CH \qquad (4\text{-}41)$$

Reaction (4-41) is faster for the neutral complexes (5 minutes) than the cationic complexes (1 hour), although for alkoxy exchange the rates are reversed, with the cationic complex exchange being complete within 24 hours and the neutral complexes showing only slight exchange over 72 hours.

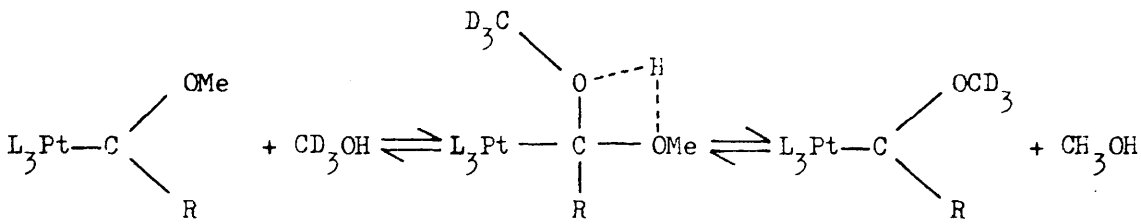
The mechanism for either type of exchange is thought to be the same

for both the charged and uncharged species. H/D exchange proceeds via proton abstraction from the α-carbon forming a vinylic intermediate (which can be isolated in some cases[57] (eqn. 4-42). Nucleophilic attack at the carbene carbon leads to alkoxy exchange (eqn. 4-43). The differences in rate have been ascribed to the change in the overall charge of the complex and a change in the cis ligand.

When cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ was dissolved in $CDCl_3/CD_3OD$ (1:1) then no H/D exchange was observed at the α-carbene carbon even after 24 hours standing. Addition of D_2O to the solution also failed to promote H/D exchange over the same time period. Similar results were



(4-42)



(4-43)

obtained with cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ and cis-$[PtBr_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ both of which did not undergo H/D exchange with alcohol. In the same experiments no alkoxycarbenes were formed indicating that no exchange of the heteroatom had occurred. The latter observation is not surprising, as the reverse reaction, aminolysis of alkoxycarbenes, has been used synthetically to prepare the cyclic aminocarbenes[125], so there appears to be a thermodynamic preference for nitrogen stabilised carbenes over oxygen.

The absence of H/D exchange suggests that the aminocarbene α-protons are much less acidic than the corresponding protons in the alkoxycarbenes. These results fit the observation that nitrogen lone pair form a better overlap with the P_z orbital on the carbene carbon[156] than oxygen, so aminocarbenes have a higher double bond character in the carbon-heteroatom bond than alkoxycarbenes. This lowers the positive charge on the sp^2 carbon in aminocarbenes and reduces the stability of a C=C double bond to the α-carbon, thus inhibiting H/D exchange by the mechanism shown in eq. (4-42). The lower acidity of the carbene protons is further shown in the low reactivity of the neutral aminocarbene complexes complexes towards bases.

Reactions with Bases

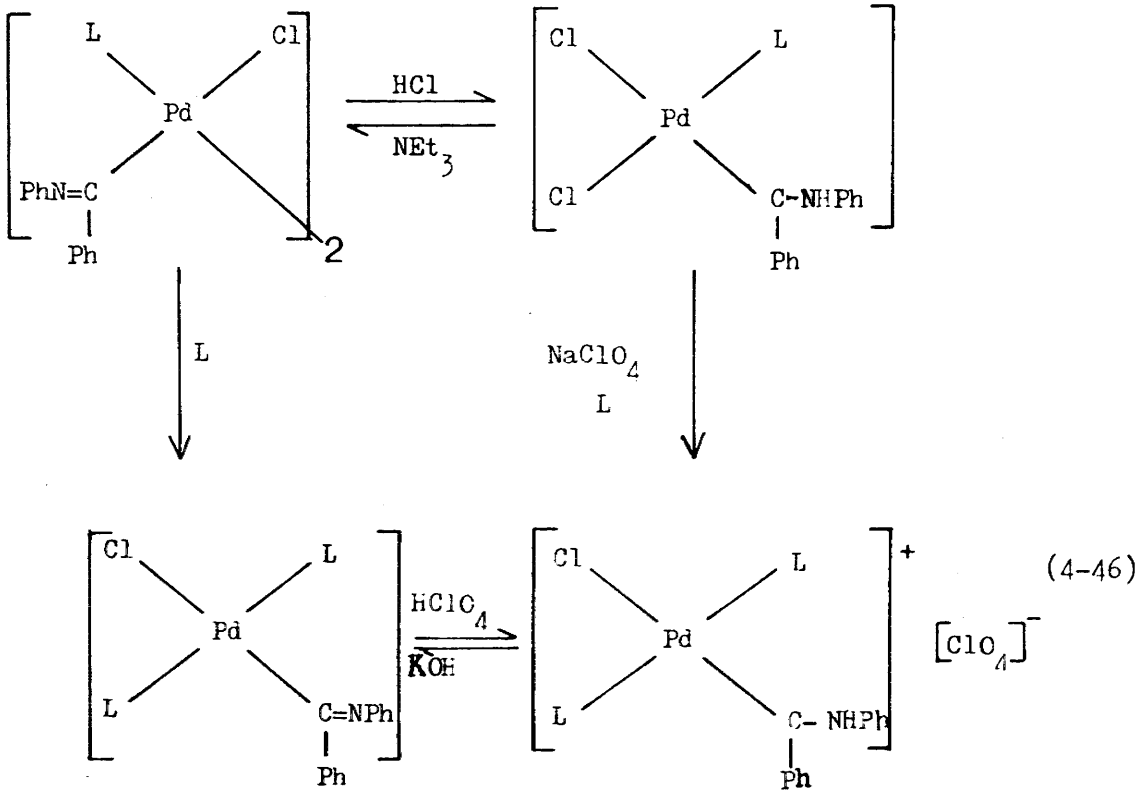
The deprotonations of a variety of platinum carbenes have been previously described. Cationic alkoxycarbenes readily lose the α-carbon proton when treated with a solution containing proton sponge (1,8-bis (dimethylamino)napthelene) or tertiary amines (eqn. 4-20).
The neutral alkoxycarbene complexes react with dimethylamine to form similar alkoxyvinyl species[123], although the reaction is accompanied by ligand exchange (eqn. 4-44). Facile reversible deprotonation of the N-H proton has also been observed in cationic complexes containing two

$$\underline{cis}\text{-}[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)] + 2\ NMe_2H \longrightarrow [PtCl(NHMe_2)\{C(OEt)=CHPh\}(PMe_2Ph)] + (NH_2Me_2)Cl \quad (4\text{-}44)$$

α-heteroatoms[158] (eqn. 4-45). In a palladium amino(organo)carbene complex again reversible de-protonation of the N-H carbene was found,

$$\underline{trans}\text{-}[Pt(CNMe)\{C(NHMe)(NPh)\}(PPh_3)_2]^+ \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [Pt(CNMe)\{C(NHMe)(NPh)\}(PPh_3)_2]^+ \quad (4\text{-}45)$$

for both neutral and cationic complexes[159] (eqn. 4-46, L = PPh_3).


L
Cl
Pd
PhN=C
Ph
2
HCl
NEt3
Cl
L
Pd
Cl
C-NHPh
Ph
L
NaClO4
L
Cl
L
Pd
L
C=NPh
Ph
HClO4
KOH
Cl
L
Pd
L
C- NHPh
Ph
+
[ClO4]-

(4-46)

When the neutral aminocarbene, cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ was treated with one equivalent of triethylamine in methanol, a white solid remained at the end of the reaction. The solvent was removed by filtration and, after evaporation, shown to contain Et_3NHCl (confirmed by comparison of its ir spectrum to that of a genuine sample.) On dissolution of the insoluble fraction into $CDCl_3$, ^{31}P nmr spectroscopy showed that many phosphorus-containing products were present. No signal was readily identifiable, although the main signal (δ -13.4, J_{PtP} 3136) has parameters very similar to cis-$[PtCl_2(CNPh)(PMe_2Ph)]$ (δ -13.6, J_{PtP} 3143). On standing in $CDCl_3$ further decomposition took place and a strong singlet at δ 34.6 grew in, due to $P(O)Me_2Ph$.

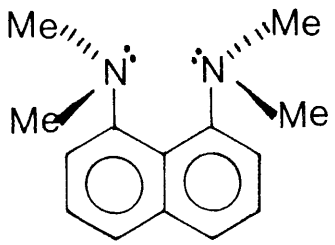
When the stronger base, alcoholic EtONa was used in place of Et_3N in the same reaction ^{31}P nmr spectrum of the product again showed that many compounds had been formed. Some, but not all, of the signals corresponded to some of the products in the reaction with triethylamine; noticeably the signals at δ -13.4 and δ 34.6 were absent in the reaction with ethoxide.

Tetrabutylammonium hydroxide similarly gave decomposition products, when allowed to react with cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ in $CDCl_3$. None of the products was readily identifiable by their ^{31}P nmr parameters.

The above three bases therefore are reacting with the platinum carbene complex, but either the initial product is unstable and prone

to further decomposition or else the bases are attacking at more than one site of the original complex. The latter seems likely, as bases could attack at the metal centre, the carbene carbon, either of the atoms in the α-position of the carbene or even by exchanging with other ligands attached to platinum.

Proton sponge (4-XVI) is known to be a strong base but a very poor nucleophile due to overlap of the nitrogen lone pairs, enforced by the



4-XVI

steric repulsions of the methyl groups. It has been used successfully in the deprotonation of cationic alkoxycarbene platinum complexes (eqn. 4-20). It was used in the present case in the hope that its low nucleophilicity would prevent the unfavourable side reactions. However, it did not react at all with cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ over a 6-day period and the starting carbene complex was recovered unaltered.

Reaction with Halides

When neutral or cationic alkoxycarbene products are allowed to react with halide ions the initial products are the acyl derivatives (eqns. 4-47, 4-48), although when the neutral complexes are used the product undergoes further decomposition[57,123]. When Et_4NCl was added to a methylene chloride suspension of cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$

$$\text{trans-}[PtCl\{C(COCH_3)CH_3\}(PMe_2Ph)_2]^+ + Cl^- \longrightarrow \text{trans-}[PtCl(COCH_3)(PMe_2Ph)_2] + CH_3Cl \qquad (4\text{-}47)$$

$$\text{cis-}[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)] \xrightarrow{\text{trace } Cl^-} \tfrac{1}{2}[Pt(\mu\text{-}Cl)(COCH_2Ph)(PMe_2Ph)]_2 + C_2H_5Cl \qquad (4\text{-}48)$$

immediate dissolution of the carbene took place leaving a pale yellow solution. After 16 hours stirring at room temperature the solvent was reduced until pale brown crystals formed which, in analysis, were found to be the starting carbene complex. So Et_4NCl has increased the solubility of the carbene complex but it has reacted reversibly with it. When followed by ^1H nmr spectroscopy in $CDCl_3$ there was no indication of any reaction and the nmr parameters were consistent with the carbene starting material. The spectrum showed resonances for N-H(δ 11.9ppm J_{HPt} 112 Hz), inequivalent benzyl methylene protons (δ 4.6, 5.1ppm, J_{HH} 14 Hz) and inequivalent phosphine methyl groups (δ 0.92, J_{HP} 11, J_{HPt} 50 Hz; δ 1.2, J_{HP} 12 Hz, J_{HPt} - obscured by other resonances). ^{31}P nmr spectroscopy showed that there was only one species in solution (δ_P -19.2 J_{PPt} 4009Hz) which from the lack of fine structure in the spectrum must have been monomeric. There was no change in any of the parameters on standing at room temperature for 72 hours. Thus the chloride must be weakly co-ordinating, most likely to platinum, at one of the vacant co-ordination sites, although co-ordination to one of the atoms on the carbene ligand must also be a possibility, especially since chloride can react with alkoxycarbene ligands. This co-ordination, like the co-ordination of methanol, increased the solubility of the complex, but it also must have been reversible, so that the less soluble starting material was isolated.

In a similar experiment, Et_4NCl did not react with cis-$[PtCl_2\{C(NHPh)CH_2Ph\}(PBu_3)]$ and the starting carbene was reclaimed in high yield (93%).

Reaction with Phosphines

Neutral alkoxycarbene platinum complexes react with free tertiary phosphine, to give products identical to those produced when the cationic complexes react with chloride[123] (eqn. 4-49), i.e. a platinum acyl complex. The first step of the reaction is thought to

be phosphine displacement of the chloride trans to the complexed phosphine,

$$\underline{cis}\text{-}[PtCl_2\{C(OMe)\ CH_2Ph\}(PMe_2Ph)] + PMe_2Ph \longrightarrow \underline{trans}\text{-}[PtCl(COCH_2Ph)\text{-}(PMe_2Ph)_2] + CH_3Cl \qquad (4\text{-}49)$$

producing a cationic alkoxycarbene complex and free chloride, which then react as shown in eqn. (4-47). Confirmation of this was provided by performing the reaction in the presence of a soluble silver salt, which removed the chloride before it could react further (eqn. 4-50) giving an isolable cationic carbene complex.

$$\underline{cis}\text{-}[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)] + PMe_2Ph + Ag(SCF_3O_3) \longrightarrow \underline{trans}\text{-}[PtCl\{C(OMe)CH_2Ph\}(PMe_2Ph)_2][S(CF_3)O_3] + AgCl \qquad (4\text{-}50)$$

When one equivalent of PMe_2Ph was added to a $CDCl_3$ suspension of $\underline{cis}$-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ dissolution of the complex took place over a period of a few minutes. ^{31}P nmr spectroscopy showed that one monomeric species was present in solution (δ_P 11.0 J_{PPt} 2553 Hz), with a coupling constant typical for two phosphines in a mutually trans environment. ^1H nmr spectroscopy (Table 4-7) showed that the benzene methylene protons were now equivalent, appearing as a 1:4:1 triplet due to coupling to platinum (δ_H=4.44 J_{HPt} = 43 Hz), but the molecule still showed hindered rotation as the phosphine methyl signals were still inequivalent. On the basis of the nmr parameters, as well as the reactions with silver salts, described below, the product of the reaction must be $\underline{trans}$-$[PtCl\{C(NHPh)CH_2Ph\}(PMe_2Ph)_2]Cl$. The complex remained unchanged in $CDCl_3$ solution over 4 days, indicating that like the neutral aminocarbene complexes, but in contrast to both neutral and cationic alkoxycarbenes, cationic aminocarbenes do not react with halide ions.

If one equivalent of silver perchlorate was added to a solution containing $\underline{cis}$-$[PtCl_2\{C(NHPh)CH_2Ph\}(PMe_2Ph)]$ to which one equivalent of

Table 4-7 Nmr parameters for $[PtCl\{C(NHPh)CH_2Ph\}(PMe_2Ph)_2]^+ A^-$

A	H					P	
	MeP			CH_2			
	δ	$^2J_{PH}$	$^3J_{PtH}$	δ	$^3J_{PtH}$	δ	$^1J_{PPt}$
Cl	1.52	~7	30	4.44	43	-11.0	2553
	1.49	~7	36				
ClO_4	1.57	~7	29	3.98	40	-10.8	2489
	1.56	~7	31				
$S(CF_3)O_3$	1.57	7.6	30	4.03	43	-10.9	2500

PMe_2Ph had been previously added then a white, light sensitive precipitate of AgCl developed. After this was removed by filtration, addition of methanol dropwise to the solution led to the isolation of white crystals of trans-$[PtCl\{C(NHPh)CH_2Ph\}(PMe_2Ph)_2][ClO_4]$. The assignment of the product was supported by elemental analysis and spectroscopic parameters (Table 4-7). Nmr spectroscopy of the product was consistent with a complex containing trans phosphine with a typical value for $^1J_{PPt}$ (2489 Hz) and the phosphine methyls appearing as a 1:4:1 triplet of triplets, due to virtual coupling[203] with both phosphorus nuclei, a phenomenon typical of mutually trans phosphines (See also Chapter 3). The carbene moiety still had hindered rotation (shown by inequivalent phosphine methyl groups). The ir spectrum contained one Pt-Cl stretch ($310cm^{-1}$) and two N-H stretches (3200, $3250cm^{-1}$), further supporting the proposed structure.

If silver triflate, $[Ag\ S(CF_3)O_3]$ was used instead of $AgClO_4$ in the above reaction then similar results were obtained (Table 4-7) although in this case the phosphine methyl proton resonances were equivalent. Since it was unlikely that rotation of the carbene ligand would be any easier for this complex than the above two, the simplicity of the Me-P signals was presumably due to chance isochrony of the resonances.

It should be noted that since the carbene still shows hindered rotation, the equivalence of the benzene methylene protons in these cationic carbenes is due to the introduction of a plane of symmetry in the molecule, by replacing one chloride with a phosphine. The plane of symmetry contains the carbene ligand, and more specifically the benzyl methylene carbon bringing the two protons attached to it into magnetically equivalent environments.

4-6.5 - Synthesis and Physical Properties of Platinum Imine Complexes

Imine compounds are well known in organic chemistry. They can be prepared simply by a condensation reaction involving a primary amine with an aldehyde or ketone. If the former is used, loss of water is spontaneous and complete; for ketones water must be removed either by distillation as the reaction proceeds or by use of drying agents. Thus the direct reaction of benzaldehyde with either $PhNH_2$ (eqn. 4-51) or $MeNH_2$ (in industrial spirits) led to the isolation of the known compounds PhN=CHPh[156] and MeN=CHPh. Similarly the reaction between ortho-

$$PhCHO + NH_2Ph \longrightarrow PhCH = NPh \qquad (4\text{-}51)$$

methylbenzaldehyde and aniline produced the new compound PhN=CH(o-tol) as a colourless liquid after being purified by vacuum distillation at high temperature (116-122°C/0.4 torr).

The platinum imine complexes were synthesised by the method of Vrieze[143]. To a solution of the halide-bridged dimer $[Pt_2Cl_4(PMe_2Ph)_2]$ was added two equivalents of the appropriate imine ligand. There was an immediate change in the colour of the solution from orange to yellow/green. After 15 minutes the solvent was removed and the crude product recrystallised from methylene chloride/pentane to yield yellow crystals of the pure imine complex. The analysis and melting points of the new complexes are presented in Table 4-8.

Spectroscopic Parameters and Stereochemistry of Platinum Imine Complexes

The ir spectra of all the imine complexes contained one Pt-Cl stretch (Table 4-9) indicative of a trans geometry of the chloride ligands. This is the same geometry as found in all other known platinum imine and amine (see section 4-6a) complexes. The C=N stretch (at $\sim 1660 cm^{-1}$) was also observable, although the presence of other bands in this region

Table 4-8 Physical data for trans-$[PtCl_2(im)(PMe_2Ph)]$

im	M.Pt(°C)	%C[a]	%H	%N
PhN=CHPh	153-155	42.79(43.08)	3.46(3.76)	2.14(2.39)
MeN=CHPh	124	36.67(36.72)	3.63(3.85)	
PhN= H(o-tol)	152-153	44.16(44.08)	3.93(4.04)	2.51(2.34)
HN=CPh_2	157-158	43.04(43.08)	3.30(3.76)	2.20(2.39)

(a) Theoretical values in parenthesis.

made a definite assignment difficult. As with the amine complexes, the value of the platinum phosphorus coupling constant (Table 4-9) was of little use in determining the product geometry due to the similarity of the observed values and those expected for either imine or chloro ligands in the trans position.

Proton nmr spectroscopy was again very useful for obtaining information about the imine complexes, and in particular the geometry around the C=N bond. As with the aminocarbenes, the Pt and H directly attached to the double bond (the imine proton) can be mutually cis or trans. Proton nmr spectroscopy shows that the geometry is trans through two/ observations -

(i) The imine proton appears as a low field doublet with platinum satellites (see fig. 4-3). The doublet was shown to be due to coupling to phosphorus by running the ^{31}P nmr spectrum of trans-$[PtCl_2(NPhCHPh)(PBu_3)]$ whilst decoupling only the aliphatic protons. The ^{31}P nmr spectrum contained a broad doublet with a P-H coupling constant (10 Hz) nearly equal to that observed for the imine proton (J = 12 Hz). The Pt-H coupling constant ($\sim$60 Hz) is very similar to that found in the monodentate diimine or iminoketone complexes where a trans geometry was shown to be preferred by crystallographic and nmr studies[161] or chelating diimines, where the geometry must be trans[149].

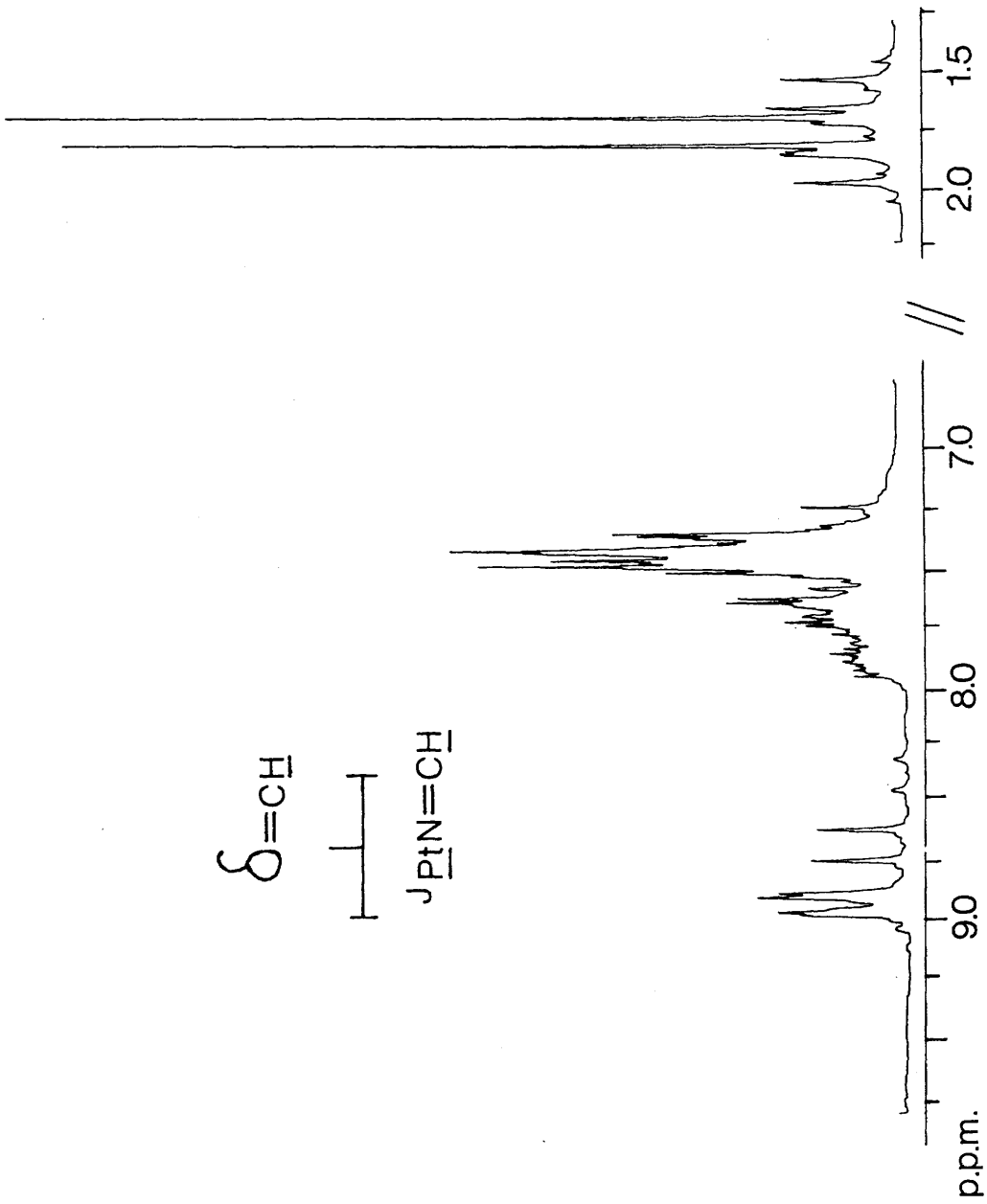
(ii) A second low field doublet of multiplets was observed at $\sim\delta$9.0. This had the intensity (by integration) corresponding to two protons when PhNCHPh was the ligand, but only one for PhNCH(o-tol). The doublet was assigned to the ortho protons on the phenyl ring attached to carbon. As mentioned in section 4-5, X-ray crystallographic studies show that there is a close approach between this proton and the metal centre. A close approach between a proton and platinum can cause a downfield

Table 4-9 Nmr parameters for Platinum Imine Complexes, trans-$[PtCl_2(im)L]$

L	im	^{31}P		^{1}H						
				MeP			H-C=N			Others
		δ	$^{1}J_{PPt}$	δ	$^{2}J_{PH}$	$^{3}J_{PtH}$	δ	$^{4}J_{HP}$	$^{3}J_{PtH}$	
PMe_2Ph	NPhCHPh	-25.5	3531	1.75	11.7	31.3	8.71	13	60	
	NPhCH(o-tol)	-24.9	3552	1.70	11.7	31.3	9.0	13	56	
	NMeCHPh	-25.9	3407	1.80	11.3	29.3	8.70	15	64	δ_{MeN} 3.36 $^{4}J_{HP}$ 2.5 $^{4}J_{HH}$ 1.5
	$NHCPh_2$	-24.9	3455	1.75	11.7	29.3	———			δ NH 9.4(br)
PBu_3	NPhCHPh	-7.8	3459	———			8.71	12	57	δ_{MeC} 2.44

Fig. 4-3 100 MHz ^{1}H n.m.r. Spectrum of

Trans-$[PtCl_2(NPh{=}CHPh)(PMe_2Ph)]$



shift in that proton's nmr resonance the size of the shift increasing as the |Pt...H| distance decreases and as the angle between the Pt...H vector and the z-axis, perpendicular to the plane of the metal decreases[143,148,163]. The doublet and further structure are due to proton-proton couplings within the aromatic ring. For the proton to be near enough to platinum to experience this deshielding effect, the phenyl ring attached to carbon must be cis to platinum, i.e. the imine proton must be trans.

The proton nmr spectrum of trans-$[PtCl_2(NMeCHPh)(PMe_2Ph)]$ was more complicated than those with phenyl groups attached to nitrogen, due to two resonances described above overlapping making assignment difficult, and a complex multiplet for the MeN group (at δ 3.9) (see fig. 4-4). Double irradiation experiments were used to simplify the spectrum. Irradiation of the signal at δ3.9 caused a sharp doublet at δ 8.7 to appear (fig. 4-4b). The increased intensity (due to removal of coupling to the N-methyl group, i.e. the signals are being sharpened from quartets to singlets) enabled observation of platinum satellites (J_{PtH} 64 Hz) and so this doublet was assigned to the imine proton. Conversely irradiation at the centre of this doublet simplified the N-methyl signal (fig. 4-4b) to a doublet (J_{PH} = 2.5 Hz) with platinum satellites (J_{HPt} 15 Hz).

Again, by analogy to the solid state structures of known imine complexes[145,161], where the imine plane is perpendicular to the plane of the platinum ligands, and from the nmr parameters, the overall structure of the platinum imine complex can be determined (4-XVI).

Fig.4-4 100MHz ^{1}H n.m.r. Spectrum of

Trans-$[PtCl_2(NMe{=}CHPh)(PMe_2Ph)]$

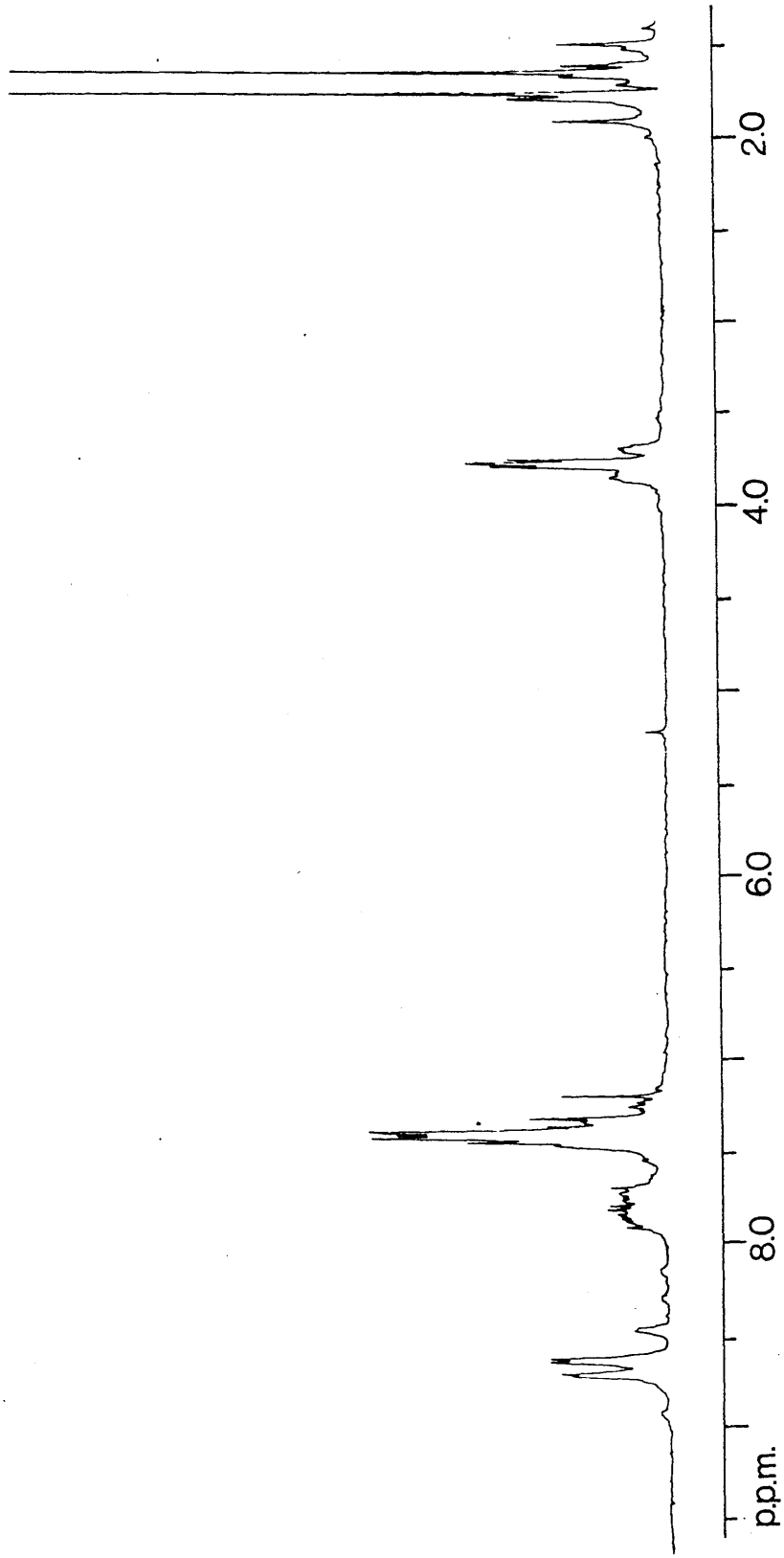
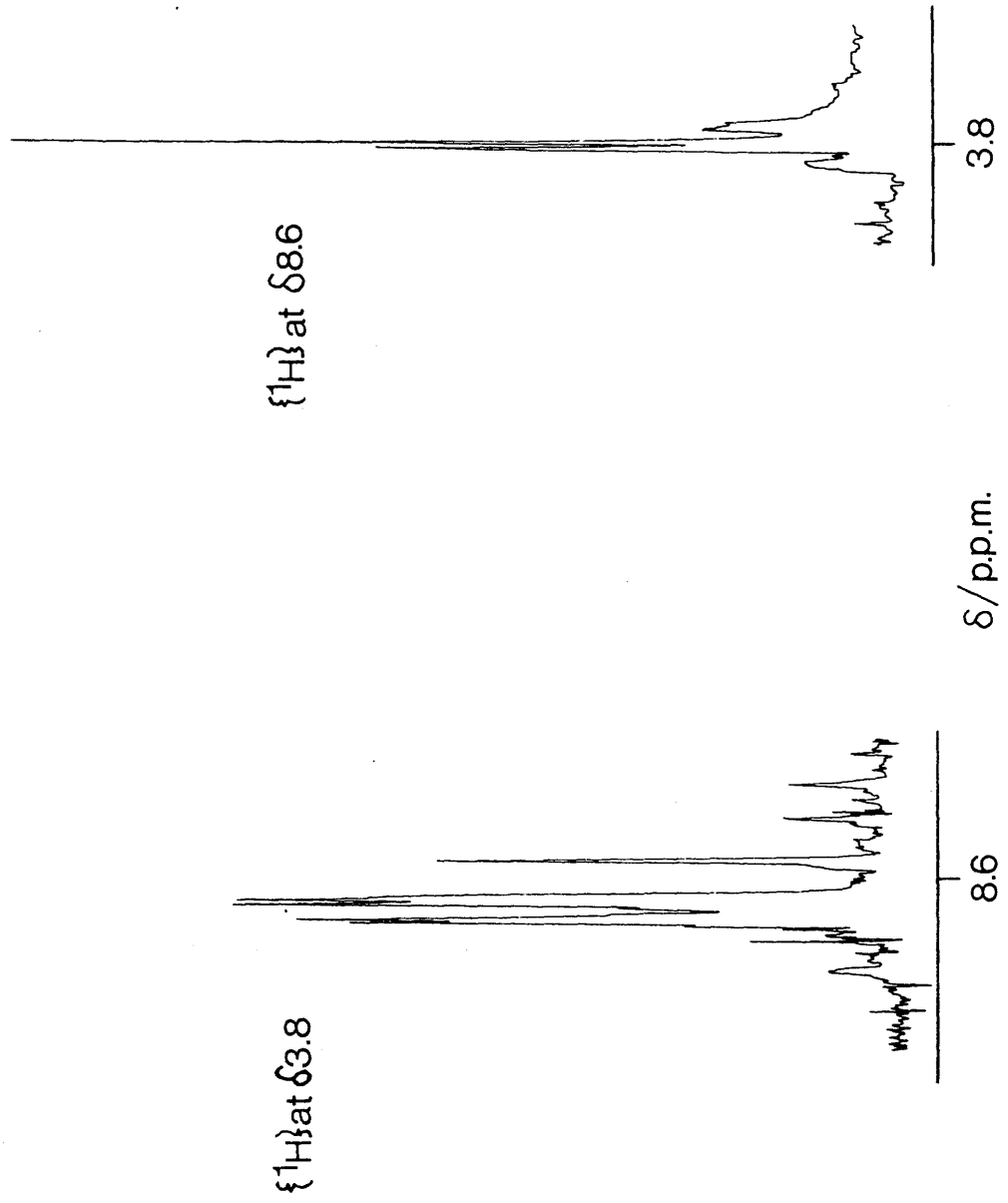
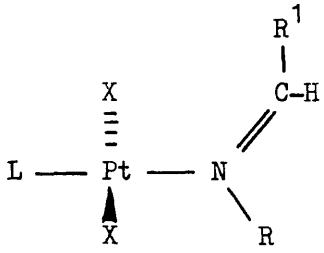


Fig. 4-4(b) Partially Decoupled ^1H n.m.r. Spectrum of

Trans-$[PtCl_2(NMe{=}CHPh)(PMe_2Ph)]$





L = PMe_2Ph; R = Ph; R^1 = Ph, o-tol

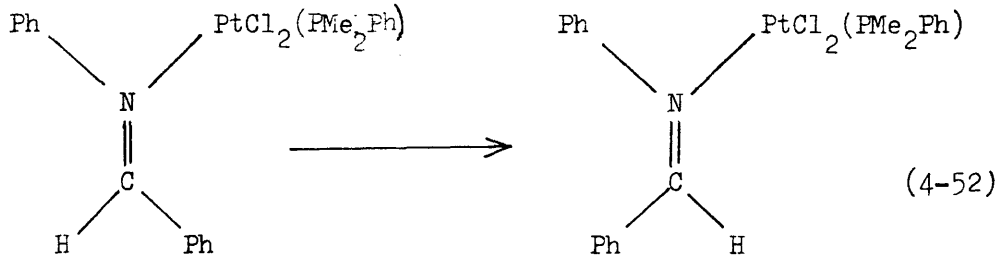
R = Me; R^1 = Ph

L = PBu_3; R = R^1 = Ph

4-XVI

Hydrolysis of Pt imine complexes

When $CDCl_3$ solutions of trans-$[PtCl_2(imine)L]$ (L = PMe_2Ph, imine = PhNCHPh, PhNCH(otol), MeNCHPh; L = PBu_3, imine = PhNCHPh) were allowed to stand, nmr spectroscopy indicated a gradual depletion of the signals for the starting complex and a new set of signals growing in. These were initially assigned to the product from an isomerisation around the C = N bond (eqn. 4-52) which was regarded as a favourable process as it placed the two bulk groups in a trans arrangement across the double bond. However, when benzaldehyde was added to a solution of trans-$[PtCl_2(NH_2Ph)$-



(4-52)

$(PMe_2Ph)]$, identical spectra were produced with evidence of trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ along with starting materials. Furthermore, from solutions of both trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ and trans-$[PtCl_2$-NPhCH(o-tol) $(PMe_2Ph)]$, yellow crystals of trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ were isolated and the aldehyde proton of PhCHO or (o-tol)CHO respectively was detected by nmr spectroscopy. It was concluded therefore that the reaction was not isomerisation but hydrolysis of the imine ligand (eqn. 4-53). An equilibrium was slowly formed, with 70% hydrolysis for complexes containing PhNCHPh or PhNCH(otol) with equilibrium being

$$\underline{\text{trans}}\text{-}[PtCl_2(NPhCHPh)(PMe_2Ph)] + H_2O \rightleftharpoons \underline{\text{trans}}\text{-}[PtCl_2(NH_2Ph)(PMe_2Ph)] + PhCHO \qquad (4\text{-}53)$$

established in around 15 days. For MeNCHPh hydrolysis proceeded to a lesser extent, being 40% complete after 50 days. $[PtCl_2(NHCPh_2)(PMe_2Ph)]$ showed no sign of hydrolysis under similar conditions indicating that the equilibrium analogous to (4-53) lies very far to the left for this ligand.

Imine Exchange Reactions.

When MeNCHPh was added to a $CDCl_3$ solution of $\underline{\text{trans}}$-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ complete imine displacement took place within a few minutes, with $\underline{\text{trans}}$-$[PtCl_2(NMeCHPh)(PMe_2Ph)]$ being formed along with free PhNCHPh. When the starting complex was treated with one equivalent of PhNCH(o-tol) an equilibrium mixture with the two imine complexes present in equimolar amounts. This reflects the basicity of the imines increasing in the order PhNCHPh $\backsimeq$ PhNCH(otol) $<$ MeNCHPh. The same order is found when P-Pt coupling constants are compared, so like the amines the more basic ligand gives a smaller value of $^1J_{PtP}$.

Reactions of Imine complexes with Bases

As discussed in the introduction it was hoped that by base assisted removal of the imine proton, new Pt-C σ-bonds could be formed. Alternatively, bases might promote ortho metallation reactions of the type that occur spontaneously at Pd (eqn. 4-26).

Amines reacted with the platinum imine complexes, but only displaced the imine ligand. So when $\underline{\text{trans}}$-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ was treated with one equivalent of either $PhNH_2$ or Et_3N, then ^{31}P nmr spectroscopy confirmed that $\underline{\text{trans}}$-$[PtCl_2(NH_2PH)(PMe_2Ph)]$ or $\underline{\text{trans}}$-$[PtCl_2(NEt_3)(PMe_2Ph)]$ were formed quantitatively. The latter amine complex was not isolated, but its spectroscopic parameters confirmed by synthesis of the same complex from $[Pt_2Cl_4(PMe_2Ph)_2]$ and Et_3N.

If stronger bases were used then there was still no reaction between the imine complex and the base. Thus the starting complex was recovered unchanged if <u>trans</u>-$[PtCl_2(NMeCHPh)(PMe_2Ph)]$ was treated with ethanolic EtONa for 14 hours or proton sponge for 48 hours.

It appears therefore that the imine complexes are highly unreactive towards bases, except N σ-donors, which can cause ligand displacement. They would therefore not be suitable precursors for the formation of organoplatinum complexes, nor can they be inter-converted with aminocarbene complexes as first hoped.

4-7 Experimental

Literature methods were used to prepare $[Pt_2Cl_4(PMe_2Ph)_2]$[163,164] $[Pt_2Cl_4(PBu_3)_2]$[165,166], (from K_2PtCl_4 and the appropriate phosphine) and PhN=CHPh[167]. $HN{=}{=}CPh_2$ was purchased from the Aldrich Chemical Company. All liquid amines were distilled prior to use. Nmr spectra were recorded in a Varian XL100 (^{31}P, ^{1}H) a Perkin-Elmer R32 (^{1}H) or a Bruker WP2003Y. I.R. were recorded on a Perkin-Elmer 530 and Perkin-Elmer 892, all solids were run as KBr discs.

Trans-dichloro(dimethylphenylphosphine)(phenylamine) platinum:- To a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (520mg, 0.64mmol) in $CHCl_3$ (50ml) under N_2. was added 4ml of $PhNH_2$ and 200µl of H≡CPh. The solution which changed colour from orange to yellow/green immediately, was stirred for 19 hours at room temperature. The solvent was removed under reduced pressure and the resulting brown oil re-crystallised from benzene/pentane to afford yellow crystals of trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ (545mg, 85%). Physical and spectroscopic parameters are given in Tables 4-1 and 4-2.

Trans-dichloro(dimethylphenylphosphine)(meta-methoxyphenylamine) platinum:- To a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (500mg, 0.62mmol) in $CHCl_3$ (50ml) was added meta-methoxyphenylamine (m-anisidine) (154mg, 1.25mmol). The solution was stirred for 24 hours. The solvent was reduced in volume (to ∿2ml) and pentane added until precipitation just began. Yellow crystals of trans-$[PtCl_2(NH_2C_6H_4OMe\text{-}m)(PMe_2Ph)]$ grew on standing (308mg, 47%). Physical and spectroscopic parameters are given in Tables 4-1 and 4-2.

Trans-dichloro(dimethylphenylphosphine)(para-nitroaniline) platinum:- This was prepared by the above method from $[Pt_2Cl_4(PMe_2Ph)_2]$ (387mg, 0.48mmol) and p-$NH_2C_6H_4NO_2$ (133mg, 0.96mmol) to afford yellow crystals of trans-$[PtCl_2(NH_2C_6H_4NO_2)(PMe_2Ph)]$, (436mg, 84%).

Trans-dichloro(dimethylphenylphosphine)(methylamine) platinum:- This was prepared similarly from $[Pt_2Cl_4(PMe_2Ph)_2]$ (506mg, 0.63mmol) and a 33% solution of $MeNH_2$ in industrial spirits (115mg of solution, containing 38mg (1.23 mmol) of $MeNH_2$) in $CHCl_3$ (20ml) to afford yellow crystals of trans-$[PtCl_2(NH_2Me)(PMe_2Ph)]$ (452mg, 84%).

Trans-dichloro(dimethylphenylphosphine)(diphenylamine) platinum:- To a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (305mg, 0.38mmol) in $CHCl_3$ (20ml) was added

$NHPh_2$ (128mg, 0.76mmol). The solution was stirred for 30 minutes, the solvent reduced in volume and pentane added until precipitation began. Orange crystals of $[Pt_2Cl_4(PMe_2Ph)_2]$ (50mg) formed on standing. These were removed by filtration and on standing yellow crystals of trans-$[PtCl_2(NHPh_2)(PMe_2Ph)]$ formed in the mother liquors (127mg, 29%). Physical and spectroscopic data are presented in Tables 4-1 and 4-2.

Trans-dichloro(diethylamine)(dimethylphenylphosphine) platinum:- To a chloroform solution (25ml) of $[Pt_2Cl_4(PMe_2Ph)_2]$ (1g, 1.24mmol) was added $NHEt_2$ (135mg, 2.53mmol). There was an immediate colour change from orange to yellow/green. After 30 minutes the solvent was removed and the resultant yellow oil re-crystallised from $MeOH/CH_2Cl_2$. White crystals of cis-$[PtCl_2(PMe_2Ph)_2]$ formed (379mg), their identity was proven by comparison of their ir and nmr spectra to that for authentic samples. The solvent was removed from the mother liquors and the resultant brown solid re-dissolved in benzene, which caused the precipitation of more cis-$[PtCl_2(PMe_2Ph)_2]$ (67mg). The benzene solution was passed through a chromatography column packed with silica gel. A yellow solution was eluted and a dark brown band remained in the column. The brown solid could not be removed from the silica even in boiling chloroform. The yellow solution was evaporated and the crude product re-crystallised from diethylether/pentane to afford yellow crystals of trans-$[PtCl_2(NHEt_2)(PMe_2Ph)]$ (298mg, 25%). Physical and spectroscopic data are presented in Tables 4-1 and 4-2.

Trans-(tert-butylamine)(dichloro)(dimethylphenylphosphine) platinum:- This was prepared by the above route from $[Pt_2Cl_4(PMe_2Ph)_2]$ (1.09g, 1.35mmol) and NH_2Bu^t (199mg, 2.72mmol). Cis-$[PtCl_2(PMe_2Ph)_2]$ was again isolated as the first product (380mg) and elution of the mother liquors through a silica gel chromatography column produced a brown

material irreversibly bound to the silica gel and a yellow solution which was evaporated and the crude product re-crystallised from $MeOH/CH_2Cl_2$ to afford trans-$[PtCl_2(NH_2Bu^t)(PMe_2Ph)]$ (52mg, 4%).

Dimethylphenylphosphine tris(methylamine)platinum dichloride:- $[Pt_2Cl_4(PMe_2Ph)_2]$ (679mg, 0.84m mol) was dissolved in $CHCl_3$ (20ml) $MeNH_2$ gas was passed through the solution for 10 minutes at ambient temperatures after which time the flask was stoppered and the solution stirred for 24 hours. There was an immediate colour change from orange to yellow/green on flowing the gas through the solution followed by the slower colour disappearance, until after 30 minutes a colourless solution remained. After 24 hours a white precipitate had formed, which was removed by filtration, affording crude $[Pt(NH_2Me)_3(PMe_2Ph)]Cl_2$ (838mg, 100%). The formula was assigned by integration of the proton nmr spectrum (recorded in CD_3OD), but the product proved impossible to purify due to amine loss on heating. Furthermore, two further attempts to repeat the reaction led only to the isolation of the bis-amine product $[PtCl(NH_2Me)_2(PMe_2Ph)]Cl$.

Chloro(dimethylphenylphosphine)bis(methylamine) platinum chloride:- Crude $[Pt(NH_2Me)_3(PMe_2Ph)]Cl_2$ was dissolved in CH_3OH and refluxed for 30 minutes. The solvent was removed leaving a brown solid which was re-crystallised from $CHCl_3$/light petroleum (60-80°C) to afford pale yellow crystals of trans-$[PtCl(NH_2Me)_2(PMe_2Ph)]$. M.Pt.172-174°C. Found C, 25.72;H,4.48;N,5.95% Calc. for $C_{10}H_{27}Cl_2N_2PPt$:- C,25.76; H,4.45; N,6.01%. ν(Pt-Cl) 283cm^{-1}, δ_P-19.2 $^1J_{PPt}$ 3987; δ_{MeP} 2.10, J_{PH} 11 Hz; δ_{MeN} 2.35 J_{HPt} 12 Hz.

The same compound was produced when $MeNH_2$ was passed through $Pt_2Cl_4(PMe_2Ph)_2$ without the formation of a precipitate, indicating that the complex can be formed without going via the tris-amine complex.

Cis-{(benzyl)(phenylamine)carbene}dichloro(dimethylphenylphosphine) platinum:- To a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (1g, 1.24mmol) in $CHCl_3$ (100ml) under N_2 was added $PhNH_2$ (255mg, 2.74mmol) followed immediately by excess $HC{\equiv}CPh$ (793mg, 7.8mmol). The solution was stirred at ambient temperatures for 7 days during which time the solution turned brown and a white precipitate of the crude product was formed, and subsequently isolated by filtration (400mg, 27%). The solid was re-crystallised from MeOH affording pure cis-$[PtCl_2\{C(NHPh)CH_2PH\}(PMe_2Ph)]$ (296mg, 20%). Analytical data are shown in Table 4-3. The original mother liquors were dried *in vacuo* and dissolved in benzene which caused precipitation of cis-$[PtCl_2(PMe_2Ph)_2]$ and growth of yellow crystals of trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$.

Cis-{(benzyl)(phenylamino)carbene}dichloro(tributylphosphine) platinum:- This was prepared similarly from $[Pt_2Cl_4(PBu_3)_2]$ (507mg, 0.54mmol), $PhNH_2$ (99mg, 1.06mmol) and $HC{\equiv}CPh$ (327mg, 3.2mmol). No precipitate formed after 7 days stirring. The solvent was reduced in volume to ~10ml and light petroleum (60-80°C) added until precipitation just began. After 3 days white crystals of cis-$[PtCl_2\{C(NHPh)/\!\!\!

Cis-{(benzyl)(meta-methoxyphenylamino)carbene}dichloro(dimethylphenylphosphine) platinum:- This was prepared similarly from trans-$[PtCl_2(NH_2C_6H_4OMe\text{-}m)(PMe_2Ph)]$ (1.042g, 1.93mmol) and $HC{\equiv}CPh$ (213mg, 2.09mmol) in $CHCl_3$ under N_2. After 7 days, a white precipitate of crude product was isolated (130mg, 14%) which was re-crystallised from CH_2Cl_2/MeOH to afford pure cis-$[PtCl_2\{C(NHC_6H_4OMe\text{-}m)(CH_2Ph)\}(PMe_2Ph)]$.

Cis-{(benzyl)(diphenylamino)carbene}dichloro(dimethylphenylphosphine) platinum:- This was prepared similarly from $[Pt_2Cl_4(PMe_2Ph)_2]$ (1g, 1.24mmol), $NHPh_2$ (416mg, 2.46mmol) and $HC{\equiv}CPh$ (510mg, 5.00mmol) in $CHCl_3$ (50ml) under N_2. After 18 hours the solution had turned black. At this point the solvent was removed and the waxy residue re-dissolved in benzene, causing precipitation of the crude product (816mg, 50%). Three successive re-crystallisations from chloroform/light petroleum (60-80°C) afforded white crystals of pure cis-$[PtCl_2\{C(NPh_2)CH_2Ph\}PMe_2Ph)]$.

Cis-{(benzyl)(phenylamino)carbene}dibromo(dimethylphenylphosphine) platinum:- To a solution of $[Pt_2Br_4(PMe_2Ph)_2]$ (500mg, 0.51mmol) in $CHCl_3$ (20ml) was added $PhNH_2$ (96mg, 1.03mmol) followed by excess $HC{\equiv}CPh$ (316mg, 3.1mmol) under N_2. The solution was stirred for 7 days during which time a white precipitate developed. This was removed by filtration giving crude product (270mg, 39%) which proved impossible to re-crystallise from either chloroform or methanol due to extremely low solubility.

Attempted synthesis of cis-$[PtCl_2\{C(NEt_2)(CH_2Ph)\}(PMe_2Ph)]$:- $[Pt_2Cl_4(PMe_2Ph)_2]$ (1g, 1.23mmol) was dissolved in $CHCl_3$ (50ml) under N_2. Et_2NH (180.2mg, 2.47mmol) was added followed by $HC{\equiv}CPh$ (516mg, 5.06mmol). On stirring for 7 days a dark brown colour developed. The solvent was removed leaving a brown oil. Re-dissolution of this oil in Et_2O produced a black precipitate (760mg) which had a complicated ^1H nmr and

ir spectra. Attempts to purify this solid appeared to lead to further decomposition.

Attempted synthesis of cis-$[PtCl_2\{C(NHBu^t)(CH_2Ph)\}(PMe_2Ph)]$:- The experimental procedure was identical to that above except Bu^tNH_2 (130.7mg, 2.48m mol). was used instead of diethylamine. Again, Et_2O re-dissolution of the crude product led to the precipitation of a black powder which proved impossible to purify further.

Similarly, attempts to prepare cis-$[PtCl_2\{C(NCPh_2)(CH_2Ph)\}(PMe_2Ph)]$ and cis-$[PtCl_2\{C(NHMe)(CH_2Ph)\}(PMe_2Ph)]$ led to decomposition and no identifiable products were isolated from these reactions.

When, instead of adding excess phenylacetylene, cis-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ was stirred in a $CHCl_3$ solution, saturated with HC≡CMe(propyne) and under a propyne atmosphere, after 7 days again a dark brown solution was formed. No solid products could be isolated from the solution.

Reaction of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$ with Et_3N:- To a suspension of the carbene complex (191mg) in MeOH (20ml) was added Et_3N (21.2mg). The suspension was stirred for 27 hours at room temperature. At the end of this period the solvent was removed. The ^{31}P nmr spectrum of the crude product in $CDCl_3$ indicated that many species were present and none of the products was identified or isolated.

Reaction of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$ with other bases:- When one equivalent of either Bu_4NOH or EtONa was added to suspensions of the carbene complex in either CH_2Cl_2 or EtOH respectively, then again ^{31}P nmr spectroscopy indicated that many phosphine containing products had been formed, and no products were isolated from either of these reactions.

When one equivalent of proton sponge was added to a $CHCl_3$ suspension of the carbene, and the mixture stirred for 6 days, then no reaction

took place and the starting materials were isolated unchanged. Proton sponge also failed to react with cis-$[PtCl_2\{C(NHPh)(PH_2Ph)\}(PBu_3)]$ under identical conditions.

Reaction of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$ with Et_4NCl:- Et_4NCl (27.6mg, 0.17mmol) was added to the carbene for 16 hours at room temperature. CH_2Cl_2 solvent was removed and the sample redissolved in $CDCl_3$. ^1H nmr showed signals for the carbene complex (δ_{CH_2} 4.63 (d), J_{HP} 11 Hz, 5.12 (d); δ_{HN} 11.85, $^3J_{PtH}$ 111 Hz; δ_{MeP} 0.92(t of d), 1.16 (t of d), J_{HPt} 50 Hz) and N-ethyl groups (δ_{CH_2} 3.35(q); δ_{CH_3} 1.18(t)). Re-crystallisation from CH_2Cl_2/MeOH produced pale brown crystals of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$.

Reaction of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$ with PMe_2Ph:- To a suspension of the carbene complex (30mg, 50.1 μmol) in $CDCl_3$ (0.5ml) was added PMe_2Ph (7.15 μl, 50.1 μmol). ^{31}P nmr spectroscopy indicated that the trans-$[PtCl\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)_2]Cl$ had been formed (see Table 4-7). This compound was stable in $CDCl_3$, and remained unchanged in solution over 6 days.

Trans-{(benzyl)(phenylamino)carbene} chloro bis(dimethylphenylphosphine) platinum perchlorate:- To a suspension of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$ (211mg, 0.35 mmol) in CH_2Cl_2 (15ml) was added PMe_2Ph (50.2 μl, 0.35 mmol) followed immediately by $AgClO_4.H_2O$ (95.5mg, 0.42 m.mol). The solution was stirred for 2 hours whilst being protected from light. AgCl was removed by filtration and the solution dried over anhydrous $MgSO_4$ and evaporated. The crude product was re-crystallised by dissolving in 3ml $CHCl_3$ and adding MeOH dropwise until precipitation just began. On standing, colourless crystals of trans-$[PtCl\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)_2]ClO_4$ formed (154mg, 46%) M.Pt. 200-202°C. Found C,44.82; H,4.52; N,1.45% Required for $C_{30}H_{37}Cl_2O_4NP_2Pt$: C, 44.95; H,4.40; N,1.75% ν(Pt-Cl) 310cm^{-1},

ν(N-H) 3200, 3250cm^{-1}. Nmr parameters in Table 4-7.

Trans-{(benzyl)(phenylamino)carbene}chloro bis(dimethylphenylphosphine) platinumtrifluoromethanesulphonate:- This was prepared, but never isolated, from the reaction of cis-$[PtCl_2\{C(NHPh)(CH_2Ph)\}(PMe_2Ph)]$ and PMe_2Ph (1:1 mole ratio) in the presence of one equivalent of $Ag[S(CF_3)O_3]$, following the above procedure. Nmr parameters of the product are given in Table 4-7.

N-Methylbenzaldehyde imine, MeN=CHPh:- $MeNH_2$ (17.86g of a 33% solution in industrial spirit, containing 5.95g, 0.19mol of $MeNH_2$) was added to PhCHO (20.00g, 0.19mol) with vigorous stirring. Heat was liberated and the mixture stirred until it had re-cooled to room temperature. The resultant orange liquid was vacuum distilled, and crude MeNCHPh collected (0.5torr, 32-36°C) as a white liquid. This was re-distilled to produce pure MeNCHPh (10.9g, 32%). ^{1}H nmr parameters were consistent with literature values[143].

N-Phenyl(2-methylbenzaldehyde) imine, PhN=CH(otol):- Ortho-methyl-benzaldehyde (6.42g, 53.5mmol) and aniline (4.98g, 53.6mmol) were added togetherwith vigourous stirring. A cloudy, viscous solution was formed very quickly (~15 secs). This was poured into 10ml EtOH/H_2O (9:1) and allowed to stand. Two liquid layers formed and separated in a funnel. The denser brown oil containing the crude product was vacuum distilled (0.4 torr, 116-122°C) to give PhN=CH(o-tol)(9.85g, 60%) as a colourless liquid. Found: C,85.83; H,6.90; N,7.52%. Required for $C_{14}H_{13}N$; C,86.11; H,6.71; N,7.17% ^{1}H (in $CDCl_3$) δ(imine proton) 8.61, δMe 2.46.

Trans-dichloro(dimethylphenylphosphine)(N-phenylbenzaldehyde imine) platinum:- $[Pt_2Cl_4(PMe_2Ph)_2]$ (300mg, 0.37mmol) was dissolved in CH_2Cl_2 (20ml). PhN=CHPh (134mg, 0.74mmol) was added. The solution changed colour from orange to yellow/green immediately. After 15 minutes the solvent was removed leaving a yellow solid which was re-crystallised

from CH_2Cl_2/light petroleum (60-80°C) to produce yellow crystals of trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ (268mg, 62%). Physical and spectroscopic data are presented in Tables 4-8 and 4-9.

Trans-dichloro(dimethylphenylphosphine)(N-methylbenzaldehyde imine) platinum:- This was prepared analogously from $[Pt_2Cl_4(PMe_2Ph)_2]$ (500mg, 0.62m mol), and MeN=CHPh (149mg, 1.25m mol) giving pure trans-$[PtCl_2(NMeCHPh)(PMe_2Ph)]$ (286mg, 44%).

Trans-dichloro(dimethylphenylphosphine)(N-phenyl(ortho-methyl)benzaldehyde imine) platinum:- This was prepared analogously from $[Pt_2Cl_4(PMe_2Ph)_2]$ (500mg, 0.62m.mol) and PhN=CH(otol) (263mg, 1.35m.mol) to give yellow crystals of trans-$[PtCl_2(NPhCH(o\text{-tol})(PMe_2Ph)]$ (661mg, 84%).

Trans-(benzophenone imine)dichloro(dimethylphenylphosphine)platinum:- This was prepared analogously from $[Pt_2Cl_4(PMe_2Ph)_2]$ (2g, 2.48m mol), and $HN=CPh_2$ (909mg, 5.02m mol) to produce yellow crystals of trans-$[PtCl_2(NHCPh_2)(PMe_2Ph)]$(2.81g, 97%).

Reaction of trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ with amines:- On addition of one equivalent of Et_3N to a $CDCl_3$ solution of the imine complex (20mg, 34.2 μmol) there was rapid displacement of the imine by amine. After 1 hour ^{31}P and ^{1}H nmr spectroscopy indicated that the only species in solution were trans- $PtCl_2(NEt_3)(PMe_2Ph)$ and unco-ordinated PhN=CHPh. Similarly when 1 drop of aniline was added to a $CDCl_3$ solution of trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ (30mg, 51.3 μmol), complete displacement took place, with trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ being the only phosphine containing product detectable by ^{31}P nmr spectroscopy.

Reactions of trans-$[PtCl_2(NMeCHPh)(PMe_2Ph)]$ with bases:- (a) EtONa:- To a suspension of trans-$[PtCl_2(NMeCHPh)(PMe_2Ph)]$ (252mg) in EtOH (25ml) was added one equivalent of freshly prepared EtONa. The suspension was stirred for 14 hours. At the end of this period unreacted starting imine

complex was removed by filtration, and analysis of the mother liquors showed that no reaction had taken place.

(b) With proton sponge:- Equimolar amounts of trans-$[PtCl_2(NMe_2HPh)(PMe_2Ph)]$ and proton sponge were allowed to react in chloroform for 48 hours. At the end of this period ^1H nmr spectroscopy showed that no reaction had taken place, with only signals for starting materials present.

Trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ + PhCHO:- To a sample of trans-$[PtCl_2(NH_2Ph)(PMe_2Ph)]$ (25mg. 50.3 μmol) in $CDCl_3$ (2.5ml) was added PhCHO(7mg, 66.0 μmol). ^{31}P nmr spectroscopy showed that trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ formed (27% in 30 minutes). The ^1H nmr spectrum was identical to that of a sample of trans-$[PtCl_2(NPhCHPh)(PMe_2Ph)]$ after it had undergone hydrolysis.

Chapter 5 - THE ISOMERISATION OF PLATINUM OLEFIN COMPLEXES $[PtX_2(olefin)PR_3]$

5-1 Introduction

Platinum olefin complexes occupy a unique position in the history of organometallic chemistry as the salt $K[PtCl_3(C_2H_4)]H_2O$, prepared by Zeise in 1827[1] and which subsequently bore his name, was the first organometallic compound reported. In more recent times a great deal of work has been performed on metal-olefin complexes due to their usefulness in catalytic processes. For example, the Wacker process (eqn. 5-1) to convert olefins to carbonyls is catalysed by palladium. The process is made catalytic by the re-conversion of Pd(0) to Pd(II) with Cu and oxygen (eqns. 5-2 and 5-3).

$$[PdCl_4]^{2-} + C_2H_4 + H_2O \longrightarrow CH_3CHO + Pd(0) + 2HCl + 2Cl^- \quad (5\text{-}1)$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl_2 \quad (5\text{-}2)$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O \quad (5\text{-}3)$$

Platinum olefin complexes are less catalytically useful than their palladium analogues (e.g. the Wacker oxidation will not occur for Zeise's salt although $[PdCl_3(C_2H_4)]^-$ is an intermediate in eqn. (5-1)). This is due to a lower reactivity of the Pt complexes, but in turn this lower reactivity makes them easier to prepare and study.

5-2 - Bonding and Stability in Pt-olefin complexes

Olefin complexes are formed in the 0 and II oxidation levels of Pt, but no Pt(IV) olefin complexes have been prepared. The properties of the platinum olefin bond are quite different in the two oxidation levels, and any description of the bonding must take into account the following experimental observations:-

1. In Pt(II) olefin complexes the axis of the double bond is perpendicular to the square plane of the platinum ligands, and rotation around the Pt-ol bond (ol = olefin) has a low energy barrier (of the order 40-65 $kJmol^{-1}$), whereas for Pt(0) complexes the olefin double bond is in the platinum-ligand plane and rigidly bound.

2. The substituents on the olefin are bent out of the plane of the double bond and away from platinum, whilst the double bond is lengthened on co-ordination. Both these effects are greater for Pt(0) than Pt(II).

The bonding is considered in terms of the Dewar-Chatt-Duncanson approach[2] involving two components. For Pt(II) olefin complexes (using the axes shown in fig. 5-1) there is firstly a σ-component from the olefin π-orbital to an empty hybrid orbital ($5d_{z^2}.5d_{x^2-y^2}.6p_z$) on platinum and a π-component from the filled 5dyz (or more strictly the $5dyz.6p_z$ hybrid) on platinum to the unoccupied π^* orbital on the olefin. This bonding scheme requires the olefin to be bound at right angles

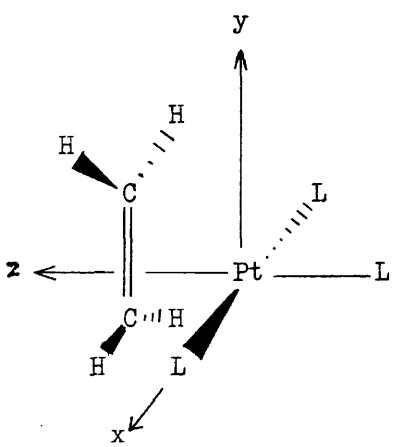


Fig. 5-1

to the square of the platinum atom. However, nmr studies have shown that rotation about the Pt-olefin bond is possible[168], and if the olefin double bond is in the platinum-ligand plane, back donation to the π^* orbitals can still occur from the $5d_{xy}$ orbital. Molecular Orbital

calculations of the total bond energy of the complex against the angle between the double bond axis and the platinum-ligand plane have shown energy minima at 90^{o} and 0^{o} [169], and it has been suggested that the preference for 90^{o} is due to the reduction of unfavourable steric interactions between the olefin substituents and other platinum ligands.

This description leads to a view of loss of electron density from the olefin π-orbital and a simultaneous increase of electron density in the π^{*}-orbital which will cause an overall weakening and lengthening of the C=C double bond. This agrees with the experimental X-ray diffraction and ir studies on these complexes. The back donation also changes the hybridisation of the carbon atoms from sp^{2} towards sp^{3}. (In the extreme case, with no σ-component and all π-back-bonding, the olefin would effectively be a dicarbanion with two completely sp^{3} hybridised carbon atoms). So the carbon atoms move towards the tetrahedral geometry expected for sp^{3} carbon atoms. When this theory was tested by MO calculations for Pt-acetylene complexes[170] it was shown that increasing electron density in the π^{*} antibonding orbitals must lead to bending of the acetylene substituents and that <u>cis</u>-bending was energetically favoured due to the steric repulsion of the central metal group. The rehybridisation of the carbon atoms will also affect the nmr coupling constants of protons on the olefin, where it is found that both J_{HH}(<u>cis</u>) and $^{3}J_{HH}$(<u>trans</u>) are decreased upon olefin co-ordination. Stability constants for Pt(II) olefin complexes are found to increase as the electron withdrawing power of the olefin substituents increases[171]. Since this change would decrease the strength of the σ-component but increase the π-component of the metal-olefin bond, the results clearly indicate that the π-component is more important in the formation of stable Pt(II)-olefin complexes.

Olefins have been found experimentally to be ligands with a very high trans effect and low trans influence[27]. This follows naturally from the above description with the bonding scheme fitting very well with the π-bonding mechanism of the trans-effect, but the low σ-donating ability leading to a low trans influence, especially if the ligand trans to the olefin exhibits little or no π-bonding itself.

Pt(C) complexes are d^{10} (although back donation from metal to ligand shall reduce this to less than 10d electrons), and typically Pt(0) olefin complexes are three co-ordinate, e.g. $[Pt(C_2H_4)(PPh_3)_2]$. Using the co-ordinate system defined in fig. 5-2 the orbitals available for the formation of π-back bonding are the $5d_{x^2-y^2}$, $5d_{z^2}$ and $6p_z$. The last two however, are used in the formation of π back bonds from Pt to the phosphine

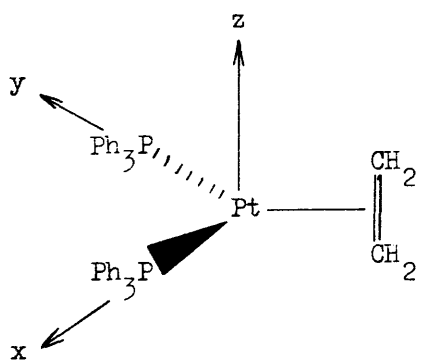


fig. 5-2

groups and no back donation can occur when the olefin is at 90° to the PtP_2 plane. Indeed MO calculations of total bond energy of the Pt-ol bond against bond angle show a minimum at 0° and a maximum at 90°(169). The σ-component from π(C=C) to the $5d_{x^2-y^2}.6p_x.6p_y$ hybrid orbital appears to have little contribution to the overall bond stability, as $(NC)_2C=C(CN)_2$ forms a strong Pt(0)-olefin bond, despite being a very poor σ-donor (although it is a strong π-acceptor).

The geometry of platinum olefin complexes can be further affected

by having bulky substituents on the olefin. Nmr studies on $[PtCl_3(C_3H_6)]^-$ and other monosubstituted olefins[168] show a slight decrease in the Pt-H coupling constant for the proton cis to the bulky group. This small difference has been interpreted in terms of a small twist round the double bond axis to minimise the non-bonding steric interactions between the olefin substituent and the metal centre (fig. 5-3).

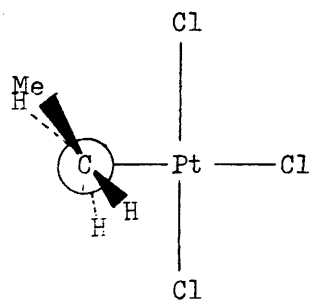
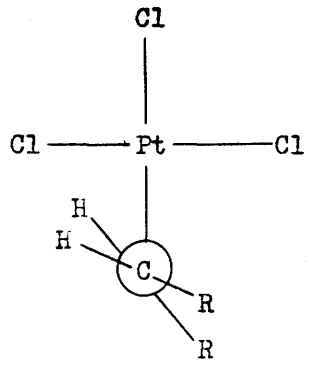
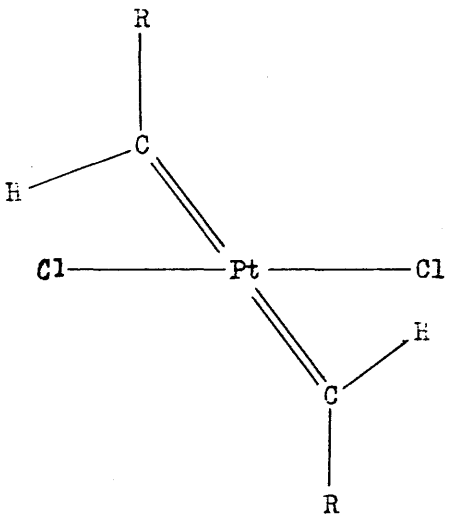


fig. 5-3

The stability constants of many Pt(II) olefin complexes have been determined[171] including disubstituted olefins[172] and it has been found that in aqueous solution they have higher stability than aquo-ligands, lower that amines and similar to Br and I. With di-substituted olefins, cis olefins form more stable complexes than trans. This is thought to be due to a combination of two reasons. Firstly, free cis olefins are more strained than their trans isomers (always excepting cyclic olefins) and the release of this strain on co-ordination will help stabilise the complexes. Secondly, cis-olefin-metal bonds are stronger than trans-olefin metal ones. This arises from two different twistings that occur to lower the destabilising steric interactions. Cis olefins will twist along the olefin double bond axis in a manner analagous to fig. 5-3 (see fig. 5-3(a) whereas trans olefins will twist around the metal olefin bond (see fig. 5-4). The latter causes a large decrease in the metal-π^* overlap and markedly



a) Rotation in cis-disubstituted olefin complexes - view along olefin double bond.



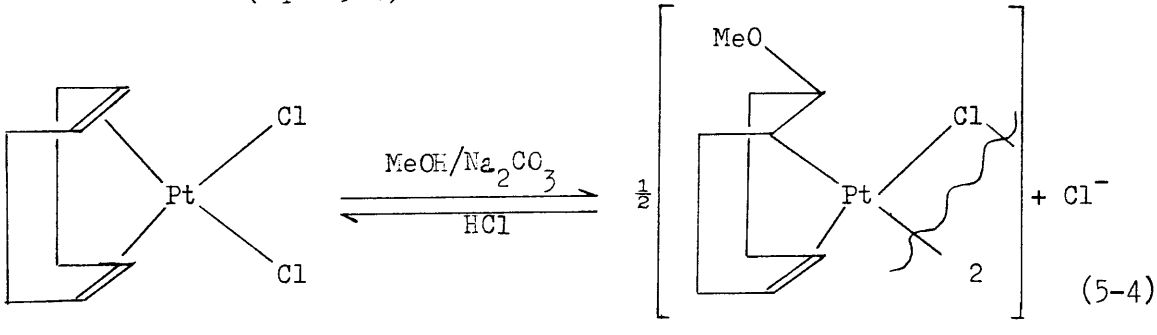
b) Rotation in trans-disubstituted olefin complexes - view along Pt-olefin bond.

Fig. 5-3(a) Rotation in substituted olefin Pt complexes.

reduce the stability of the complex, whilst the former has much less effect on the back bonding and mostly affect the σ-component which is of far less importance to the overall stability of the complex.

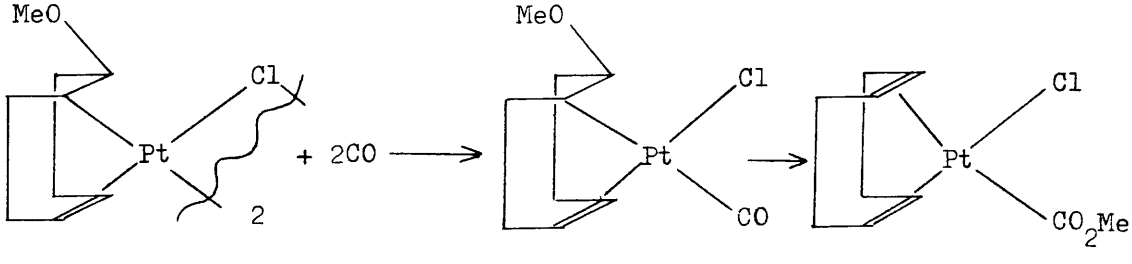
5-3 - Chemical Reactivity of Pt-Olefin Complexes

Although Pt(II) olefin complexes are chemically less reactive than their Pd(II) analogues (e.g. the Wacker process (eqn. 5-1) occurs spontaneously in water, but Zeise's salt does not react with water until 100°C, and even then decomposition, with liberation of ethene, is predominant[173]) they are still susceptible to nucleophilic attack. When alkoxide ions attack monoolefin complexes decomposition usually occurs, but with diolefin complexes, olefin-alkylplatinum(II) complexes are formed[13] (eqn. 5-4).



(5-4)

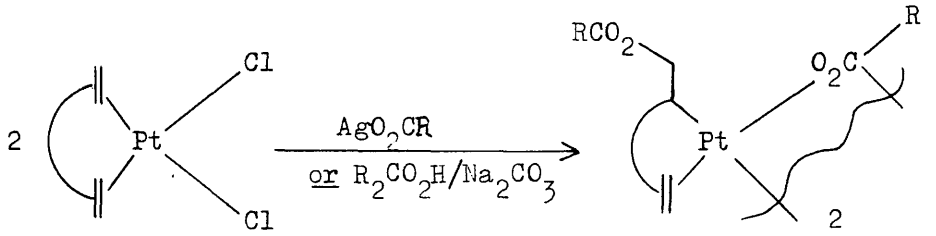
The reaction can be reversed by boiling the product in hydrochloric acid. The product also reacts with CO which will split the halide bridge to form the Pt-carbonyl species, or react further to reform the diolefin[174] (eqn. 5-5). Whether or not the second step occurs depends strongly on the electrophilic character of the diolefin.



(5-5)

Carboxylate anions react with diolefin-platinum(II) complexes in a

similar manner to alkoxides[175] with the formation of a Pt-C σ-bond (eqn. 5-6, diolefin=cyclooctadiene, norbornadiene). Studies in the

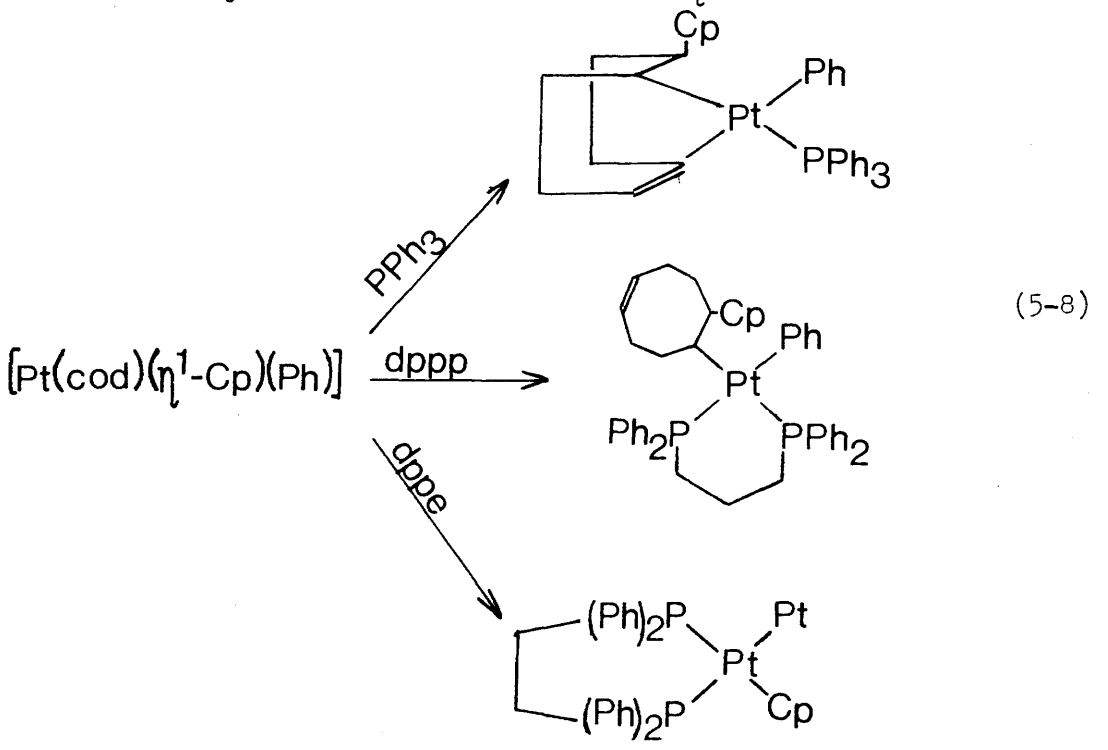


(5-6)

ligand[175b] have shown that both with alkoxides and carboxylates, the nucleophile attacks the double bond on the side <u>trans</u> from Pt, as would be expected on steric grounds.

Internal nucleophilic attack on diolefins has also been observed[176] although the nature of the product depends on the nucleophile and the supporting ligands (eqn. 5-7, 5-8).

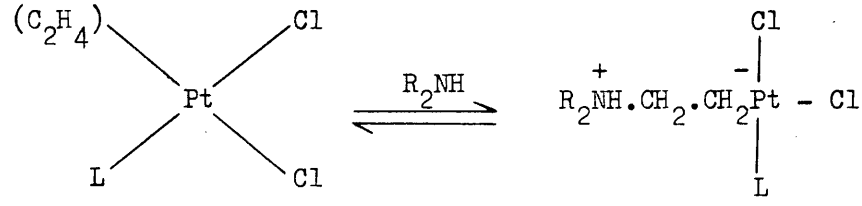
(5-7)



(5-8)

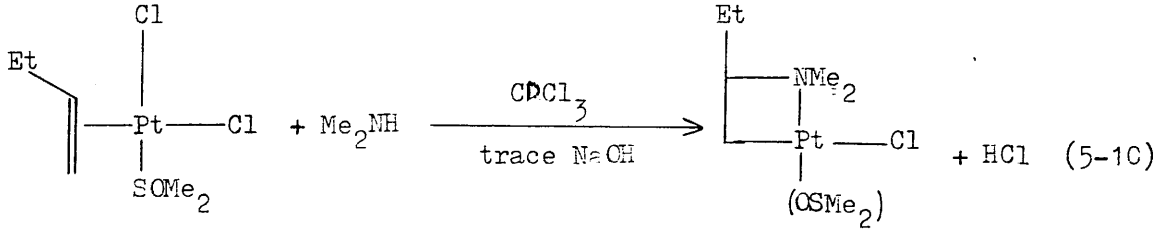
Amines attack diolefins in a similar manner, but they also react with monoolefin complexes to form zwitterionic complexes[177] (eqn. 5-9,

L = PR_3 or NR_3) with the equilibrium position being very dependent on the



(5-9)

bulk of the amine with the σ-bonded complex being favoured by small, unhindered amines[178]. When excess amine is reacted with cis-$[PtCl_2(C_2H_4)(amine)]$, the first product is still the zwittenonic complex as shown in eqn. (5-9), but the excess amine will displace one chloride to form $[PtCl(amine)_2\ CH_2CH_2(amine)H]^+$[171]. In the presence of a base the aliphatic ligands can be made to cyclise forming a four membered ring (eqn. 5-10, L = PR_3,NR_3,dmso)[180].



(5-10)

5-4 - Preparation and stereochemistry of Pt-olefin complexes

The geometry of the ligands around platinum in the complexes $[Pt(olefin)L_3]$ will depend both on the type of ligands present and the synthetic route employed. The latter point can be illustrated in the synthesis of cis and trans-$[PtCl_2(C_2H_4)(NHEtPh)]$ (eqn. 5-11, 5-12).

$$K_2[PtCl_4] + NHEtPh \longrightarrow K[Pt(NHEtPh)Cl_3] \xrightarrow{C_2H_4} \text{cis-}[Pt(NHEtPh)(C_2H_4)Cl_2] \qquad (5\text{-}11)$$

$$K[PtCl_3(C_2H_4)] + NHEtPh \longrightarrow \text{trans-}[PtCl_2(NHEtPh)(C_2H_4)] \qquad (5\text{-}12)$$

One of the most common methods of preparing olefin complexes has been the cleavage of halide-bridged diplatinum complexes either by olefin, or else incorporating olefin into the bridged complex and cleaving the

bridge with another ligand (eqns. 5-13[181], 5-14[182], am = 2,4,6-trimethylpyridine).

$$\left[Pt_2Cl_4(PR_3)_2\right] + 2CH_2{=}CH.CH_2OH \longrightarrow 2\ \underline{cis}\text{-}\left[PtCl_2(CH_2{=}CHCH_2OH)(PR_3)\right] \quad (5\text{-}13)$$

$$\left[Pt_2Cl_4(C_2H_4)_2\right] + 2\ am \longrightarrow 2\ \underline{trans}\text{-}\ PtCl_2(am)(C_2H_4) \quad (5\text{-}14)$$

As shown in equation (5-13), platinum phosphine olefin dihalide complexes are invariably cis although in the reaction between $\left[Pt_2Cl_4(PPr^n_3)_2\right]$ and $CH_2{=}CHCH_2OH$ at low temperature, trans-$\left[PtCl_2(CH_2{=}CHCH_2OH)(PPr^n_3)\right]$ was shown to be the first product, which disappeared rapidly on warming to room temperature being replaced by the cis isomer[131] Similar results were achieved between $\left[Pt_2Br_4(PMe_2Ph)_2\right]$ or $\left[Pt_2Cl_4(PMe_2Ph)_2\right]$ and allyl alcohol, with the trans→cis isomerisation being found to be faster for the bromo complexes. With the very bulky phosphine complex $\left[Pt_2Cl_4(PPr^nBu^t_2)_2\right]$ allyl alcohol again split the halide bridge at low temperature to form trans-$\left[PtCl_2(CH_2{=}CHCH_2OH)(PPr^nBu^t_2)\right]$ but, due to the bulk of the phosphine, the cis complex could not be formed and the composition of the solution at room temperature was not reported.

Reactions of CO with $\left[Pt_2X_4(PR_3)_2\right]$

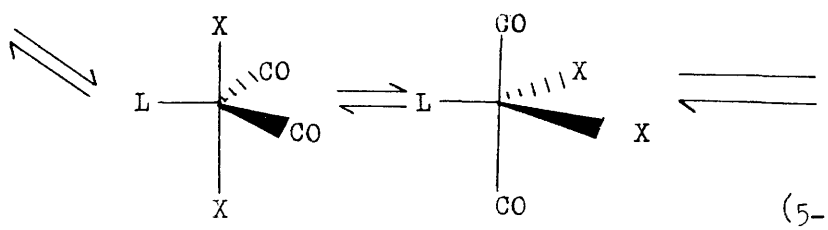
The reactions of CO with $\left[Pt_2X_4(PR_3)_2\right]$ (X = Cl, PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, PBu_3, PCy_3; PR_3 = PMe_2Ph, X = Br, I)[106] have been studied recently by Anderson and Cross. They found the initial cleavage of the dimer by CO lead to rapid formation of the expected trans-$\left[PtX_2(CO)L\right]$ which then slowly isomerised (1-3 days) to the cis-form. The isomerisation stopped at temperatures below -30°C. In some cases (X = Cl, L = $PMePh_2$, PPh_3) by freeze-drying from benzene solutions, the pure trans isomers could be isolated. In solution, the trans isomers tended to lose CO, and on sweeping the solutions with N_2, total re-dimerisation due to CO loss occurred within 5 hours.

The isomerisation rate is dramatically increased when excess CO is present. For instance, a solution of trans-$[PtCl_2(CO)(PMePh_2)]$ was completely converted to the cis isomer in 35 minutes when a flow of CO was maintained through the solution, although an identical untreated solution was unchanged over the same time period. (With bulky phosphines, such as $P(C_6H_{11})_3$ no isomerisation occurred even after prolonged treatment with CO[183]). By using ^{13}C-labelled CO, it was shown that CO exchange occurs for both isomers, although it was faster for the trans isomer (50% exchange after 15 minutes) than for the cis isomer (30% exchange in 1 hour).

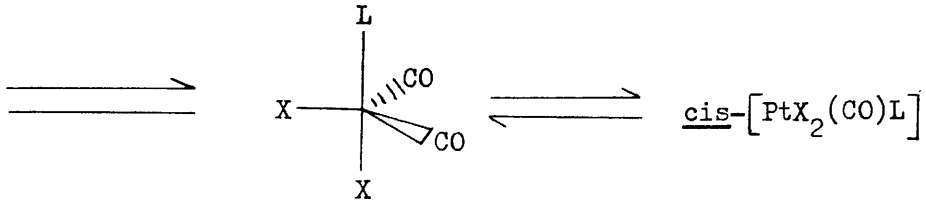
Other nucleophiles catalyse the isomerisation. Free phosphine was as effective as CO at increasing the rate whereas halide ions (Cl^-, Br^- and I^-) acted more slowly. It is thought that for uncatalysed isomerisations, the partial loss of CO from the trans isomer provides the catalyst for the isomerisation which would then proceed via a 5-co-ordinate associative intermediate undergoing pseudo-rotation (eqns. 5-15, 5-16). It should be noted that intermediates (A) and (B) in eqn. (5-16) are those that would be involved in the sterospecific exchange of CO in the trans and cis isomers respectively.

Due to the similarity of Pt-L bonding between L = CO and L = C_2H_4, it was thought that a similar study of olefin analogues would yield similar results and give more information about both systems. In this chapter it will be shown that the formation and isomerisation of $[PtX_2(ol)L]$ is considerably more complicated than for the carbonyl complexes.

$$\text{trans-}[PtX_2(CO)L] \rightleftharpoons [PtX_2L] + CO \qquad (5\text{-}15)$$

trans- $PtX_2(CO)L$ 

(5-16)



$\underline{cis}$-$[PtX_2(CO)L]$

5-6 - Results and Discussion

5-6.1 - The reactions of ethene and propene with $Pt_2X_4L_2$

The overall reaction being studied can be represented by eqn. (5-17). The starting complexes $[Pt_2Cl_4(PMe_2Ph)_2]$, $[Pt_2Br_4(PMe_2Ph)_2]$ and

$$[Pt_2X_4L_2] + 2ol \longrightarrow 2\ \underline{cis}\text{-}[PtX_2(ol)L] \qquad (5\text{-}17)$$

$[Pt_2Cl_4(PBu_3)_2]$ are all well characterised compounds. The latter by boiling in acetone with either KBr or LiI was readily converted to the complexes $[Pt_2Br_4(PBu_3)_2]$ and $[Pt_2I_4(PBu_3)_2]$ respectively. The latter, although investigated in detail by ^{31}P nmr spectroscopy[184] had not previously been isolated, whereas the bromo complex is new. The ^{31}P nmr spectrum of the bromo complex could be analysed as for the other halides and the coupling constants are shown in Table 5-1. Reaction of the appropriate halide complex with C_2H_4 or C_3H_6 produced white crystalline complexes $\underline{cis}$-$[PtCl_2(C_2H_4)(PMe_2Ph)]$[185], $\underline{cis}$-$[PtCl_2(C_3H_6)(PMe_2Ph)]$, $\underline{cis}$-$[PtBr_2(C_2H_4)(PMe_2Ph)]$, $\underline{cis}$-$[PtCl_2(C_2H_4)(PBu_3)]$[186] and $\underline{cis}$-$[PtBr_2(C_2H_4)(PBu_3)]$. Physical data for the new complexes are shown in Table 5-2. The dimethylphenylphosphine complexes are very insoluble in chloroform and were isolated as pure crystals directly from the reaction vessel when a slow stream of olefin was passed through a solution of $Pt_2X_4(PMe_2Ph)_2$. With the more soluble PBu_3 complexes the chloro complex was crystallised by maintaining a stream of ethene to remove chloroform by evaporation, and the bromo complex by addition of light petroleum to a chloroform solution of the compound. These olefin complexes exhibit a typical coupling constant between platinum and the

Table 5-1. ^{31}P nmr parameters of $[Pt_2X_4(PBu_3)_2]$

X	δ_P	$^1J_{PPt}$	$^2J_{PtPt}$	$^3J_{PPt}$	$^4J_{PP}$
Cl	3.57	3741	199	23.5	2.8
Br	1.73	3679	230	25.4	3.4
I	1.49	3425	380	21.4	5.1

Table 5-2 Physical Data for complexes cis - $[PtX_2(ol)L]$

L	ol	X	M.Pt (℃)	%C	%H	Others
$PEtPh_2$	C_3H_6	Cl	160-171 (dec)	29.63(29.61)	3.80(3.84)	Cl:15.2(15.89)
	C_2H_4	Br	120-140(dec)	22,75(23.05)	2.54(2.90)	Br:31.23(30.67) P:6.18(5.94)
PBu_3	C_2H_4	Cl	110-117(dec)	34.09(34.37)	5.30(4.94)	Cl:13.46(14.50)
		Br	95-100(dec)	28.55(29.08)	5.34(4.18)	Br:27.50(27.64)

olefin protons (J_{PtH} = 61Hz) whilst J_{HP} (<1.5Hz) is consistent with a cis geometry. The dichlorocomplexes also exhibit two Pt-Cl stretches in their ir spectra confirming the cis geometry. The ^{31}P nmr parameters of these and other complexes are shown in Table 5-3. All the complexes were thermally unstable, decomposing on heating and eventually melting to give red/orange liquids whose subsequent "re-melting" points showed them to be the starting dimers. Due to the extremely low solubility of the dimethylphenylphosphine complexes, most of the subsequent studies were performed on the PBu_3 compounds with which no such solubility problems were encountered.

It was found that passing olefin through solutions of cis-$[PtCl_2(ol)(PBu_3)]$ caused rapid stereospecific olefin exchange. Thus C_3H_6 would completely displace ethene from cis-$[PtCl_2(C_2H_4)(PBu_3)]$ within one minute at room temperature to give the propene complex, whilst the treatment of the product with ethene caused the reverse reaction (eqn. 5-18). Adding propene for a very short time (4.5) produced a mixture of

$$\text{cis-}[PtCl_2(C_2H_4)(PBu_3)] \underset{C_2H_4}{\overset{C_3H_6}{\rightleftharpoons}} \text{cis-}[PtCl_2(C_3H_6)(PBu_3)] \quad (5\text{-}18)$$

the two olefin complexes containing 30% of the propene complex, although in this case the exchange was not as rapid due to the lower concentration of free olefin present. It is notable that the exchange is much faster than for the carbonyl complexes, where 1 hour of CO treatment was required to effect 30% exchange in cis-$[PtCl_2(CO)(PMePh)_2]$. This type of olefin exchange has been used synthetically to prepare new Pt-olefin complexes such as cis-$[PtCl_2(C_3H_6)(PBu_3)]$ and cis-$[PtCl_2(C_4H_8)(PBu_3)]$ from the ethene complex[187], although the experimental conditions used (12 hours of C_3H_6 in refluxing CH_2Cl_2) seem a bit excessive in view of the above results.

Table 5-3 ^{31}P nmr parameters of Pt-olefin complexes $[(PtX_2(ol)L]^{(a)}$

L	X	ol	cis isomer δ	cis isomer J	trans isomer δ	trans isomer J
PMe_2Ph	Cl	C_2H_4	-10.0	3091		
			(-8.0)	(3090)	(-10.0)	(3467)
	Br	C_2H_4	-9.3	3010		
			(-6.5)	(3006)	(-12.2)	(3343)
PBu_3	Cl	C_2H_4	5.0	3041	5.8	3440
			(7.2)	(3054)	(6.0)	(3383)
		C_3H_6	4.1	3088	5.3	3459
		C_7H_{14}	3.6	3089	4.7	3468
					(5.2)	(3364)
	Br	C_2H_4	5.2	2964	3.8	3346
			(7.5)	(2962)	(4.0)	(3265)
		C_3H_6			(2.5)	(3298)

(a) Recorded at room temp. (or -60°C)

The greater reactivity of cis-Pt olefin complexes over analogous carbonyl compounds was also apparent in other types of reaction. So, for instance, cis-$[PtCl_2(CO)L]$ was stable in $CHCl_3$ solution, and passing N_2 gas through the solution for 5 hours, had no effect on the complex, indicating that there was no CO loss from these complexes in solution. The olefin complex cis-$[PtCl_2(C_2H_4)(PBu_3)]$ slowly lost olefin until it had completely re-dimerised after 4 days, with the reaction being rapidly accelerated by passing N_2 through the solution (40% re-dimerisation after 2 hours N_2). The bromo complexes cis-$[PtBr_2(C_2H_4)(PMe_2Ph)]$ and cis-$[PtBr_2(C_2H_4)(PBu_3)]$ were much less stable, re-dimerising rapidly at room temperature, with the process being complete within 30 minutes (for L = PBu_3). Again, sweeping the solutions with N_2 gas hastened the reaction so that olefin loss from the PBu_3 complex was complete within 5 minutes. The result of these reactions is that, at least for X = Br, cis$[PtX_2(ol)L]$ is not the "final product" of the reaction represented by eqn. (5-17) and that re-conversion to the dimer at a rate similar to its formation, must always be allowed for. The bromo complexes would be expected to re-dimerise more readily, as the strength of the halide bridge in the diplatinum complexes increases in the order Cl < Br < I. The lower stability of olefin complexes over carbonyl ones has been reported already[186].

The cleavage of the halide-bridged dimer $[Pt_2X_4L_2]$ by a nucleophile (Nu) would be expected to give complexes of the type trans-$[PtX_2LNu]$ as the initial product due to the higher trans effect of the phosphine ligand L over halide X. This was found to be the case when amines attacked the halide bridge producing stable trans-$[PtX_2(am)L]$ (see chapter 4). If the trans form is the less stable isomer then further isomeration to cis can occur. When the reactions of

$[PtX_4(PBu_3)_2]$ (X = Cl,Br) with C_2H_4 or C_3H_6 were followed by ^{31}P nmr spectroscopy, the appearance of new signals before the formation of cis isomer was detected. From the appearance of a simple 1:4:1 triplet pattern in the spectra, it was clear that these complexes were mono-platinum complexes. (Dimeric complexes would give 19 signals in the ^{31}P nmr spectrum (see Table 5-1). These signals were therefore assigned to trans-$[PtX_2(ol)L]$. This assignment was supported by the similarity of the PtP coupling constants (see Table 5-6) with trans-$[PtCl_2(CH_2=CHCH_2OH)(PPr_3)]$[181] ($J_{PtP}$ 3323 Hz) and trans-$[PtCl_2(CH_2=CHCH_2OH)(PMe_2Ph)]$ (J_{PtP} 3441 Hz). The values are larger than for the trans carbonyl complexes ($^1J_{PtP}$ 2900) indicating that the CO ligand has a higher trans influence than the olefin ligand.

The formation of the trans-carbonyl complexes is complete in solution, and they can, in some cases, be isolated as pure compounds and their reactions studied[106]. Unfortunately the trans olefin complexes rapidly form equilibria with the dimers (eqn. 5-19, R = H,Me) so pure solutions of the trans- complex at temperatures which they would

$$Pt_2X_4(PBu_3)_2 + 2\ CH_2=CHR \underset{}{\overset{K}{\rightleftharpoons}} 2\ \text{trans-}[PtX_2(CH_2=CHR)(PBu_3)] \qquad (5\text{-}19)$$

further react were not available.

Several attempts were made to isolate a trans complex, using the less soluble PMe_2Ph. The first attempts involved freeze drying benzene solutions of $[Pt_2Cl_4(PMe_2Ph)_2]$ saturated with C_2H_4, but only dimer was isolated, probably due to olefin loss at low pressure. The other method employed involved treating a solid sample of $[Pt_2Cl_4(PMe_2Ph)_2]$ with gaseous C_2H_4. The dimer was prepared in a finely divided form again by freeze drying from benzene. Treatment of the solid with ethene for 6 and 10 hours produced a change in the carbon analysis, suggestive of

some olefin complex formation (see Table 5-4) but on re-dissolution of the solid in $CDCl_3$ only dimer was present (as shown by ^{31}P nmr spectroscopy). It seems likely that the increase in amount of carbon could be from non-volatile impurities in the gas. These failures show again that, like the cis complex, the trans olefin complexes have a lower stability than the corresponding carbonyl complexes.

At -60°C pure solutions of trans-$[PtCl_2(C_2H_4)(PBu_3)]$ could be formed, due to the effect of temperature dependance of equilibrium(5-19). At this temperature the complex showed no sign of isomerisation or olefin loss over 1 hour. However, on warming the solution up to -20°C olefin loss became apparent and the presence of dimer could be detected. At 0°C isomerisation to the cis form was also observed. Although no olefin loss was observed at -60°C, dissociation must take place, as sweeping a solution of trans-$[PtCl_2(C_2H_4)(PBu_3)]$ with N_2 at -60°C caused redimerisation with the olefin loss being complete between 40 and 60 minutes. Passing nitrogen through solutions of trans-$[PtX_2(ol)(PBu_3)]$ (X = Cl, ol = C_2H_4, C_3H_6, X = Br, ol = C_2H_4) or trans-$[PtX_2(ol)(PMe_2Ph)]$ (X = Cl,Br; ol = C_2H_4) at room temperature completely removed the olefin in less than one minute.

Olefin exchange was rapid with the trans complexes, even at -60°C. Treatment of solutions of trans-$[PtCl_2(C_2H_4)(PBu_3)]$ at -60°C with C_3H_6 caused complete olefin exchange within 2 minutes, producing trans-$[PtCl_2(C_3H_6)(PBu_3)]$, a reaction that could be reversed by treating the latter complex, still at -60°C,with ethene (eqn. 5-20).

$$\text{trans-}[PtX_2(C_2H_4)(PBu_3)] \underset{C_2H_4}{\overset{C_3H_6}{\rightleftharpoons}} \text{trans-}[PtX_2(C_3H_6)(PBu_3)] \qquad (5\text{-}20)$$

With the corresponding bromo complexes the reaction was more complicated. Treatment of $[Pt_2Br_4(PBu_3)_2]$ with C_2H_4 for 2 minutes,

Table 5-4 Effect of C_2H_4 on solid $\left[Pt_2Cl_4(PMe_2Ph)_2\right]$

		%C	%H
$\left[Pt_2Cl_4(PMe_2Ph)_2\right]$	Calculated	23.78	2.74
	Precipitated benzene	23.4	2.2
	After 6 hours of ethene	24.5	2.3
	After 10 hours of ethene	25.68	2.17
$\left[PtCl_2(C_2H_4)-(PMe_2Ph)\right]$	Calculated	27.79	3.50

followed by cooling to -60°C produced a solution containing roughly equal amounts of starting dimer and trans-$[PtBr_2(C_2H_4)(PBu_3)]$ with a trace of the cis isomer. This reflects both the increased strength of the halide bridge with Br over Cl and also a faster trans $\longrightarrow$ cis isomerisation rate for bromo complexes. Treatment of this mixture with propene at -60°C for 2 minutes gave a solution of nearly pure trans-$[PtBr_2(C_3H_6)(PBu_3)]$ with no dimer present. (The amount of cis isomer was very low and its presence could not be accurately determined). Again, reversing the process gave trans-$[PtBr_2(C_2H_4)(PBu_3)]$ and with long accumulation time the ^{31}P nmr spectrum showed the presence of the cis isomer. The fact that the dimer was cleaved by propene at low temperature is interesting as there is no reaction between the two compounds at room temperature. The change reflects the fact that at -60°C propene is a liquid and so was present in very high concentration, and the lower temperature would increase the stability of the trans complex. The cleavage of $[Pt_2Br_4(PBu_3)_2]$ by C_2H_4 also would take place at -60°C, and in this way pure solutionsof trans-$[PtBr_2(C_2H_4)(PBu_3)]$ could be prepared.

It seems certain that these exchange reactions (eqns. 5-18, 5-20) are associative. Although olefin loss to reform the bridged diplatinum species is possible, the time taken to remove the olefin with N_2 is considerably longer than for the exchange reactions. Associative reactions involving 5 co-ordinate intermediates, however, are well known[23] and this mechanism is also thought to be the mechanism of carbonyl exchange in the analogous reactions with carbon monoxide[106].

As stated before (eqn. 5-19) the initial treatment of halide-bridged diplatinum species leads to an equilibrium being established between the dimer and the trans olefin complex:-

$$Pt_2X_4(PBu_3)_2 + 2\ ol \overset{K}{\rightleftharpoons} 2\ \underline{trans}\text{-}[PtX_2(ol)(PBu_3)] \qquad (5\text{-}19)$$

The position of this equilibrium might be expected to have an effect on the rate of formation of the cis isomer, and the factors affecting the system were looked at. The equilibrium ratio was found to be very dependent on experimental conditions and found to be sensitive to such factors as temperature, type of halide or olefin and light.

Lowering the temperature, as expected from the entropy of the system, moves equilibrium (5-19) to the right, so that at -60°C pure trans-$[PtCl_2(ol)(PBu_3)]$ (ol = C_2H_4, C_3H_6) can be obtained, but at room temperature the equilibrium (in the light) shows 80% dimer for ol = C_2H_4 and 56% for C_3H_6. The bromo complexes of ethene also exhibit this change although a sample containing pure trans-$[PtBr_2(C_2H_4)(PBu_3)]$ at -60°C changed to 95% dimer at room temperature (see Table 5-5).

The nature of the halide also had the expected effect, halide bridge cleavage being favoured by Cl over Br for either PBu_3 and PMe_2Ph complexes with the iodo bridged dimers neither ethene or propene formed olefin complexes at room temperatures. These results are consistent with the halide bridge strength decreasing in the order I > Br > Cl.

With X = Cl, equilibrium (5-19) lies further to the right when ol = C_3H_6 than ol = C_2H_4 (see Table 5-5, Figs. 5-4, 5-5). This reflects the higher nucleophilicity of propene due to the electron releasing methyl group causing a higher π-electron density in the olefin double bond. With X = Br only ethene causes cleavage of the halide bridge. As mentioned in the introduction, electron releasing groups decrease the strength of the Pt-ol bond and so ethene complexes would be expected to be more stable than propene ones, so the reaction must be under thermodynamic control. With all other olefins, cleavage of the bridge

Table 5-5 Effect of olefin on $[Pt_2X_4(PBu_3)_2]$ (a)

X	Temp. (°C)	ol = C_2H_4 (b)	C_3H_6
Cl	20	19	61
	-60	100	100
Br	20	5	0
	-60	50	0

(a) Recorded after 1 minute olefin at room temperature through a $CDCl_3$ solution of $[Pt_2X_4(PBu_3)_2]$

(b) Results expressed as % [trans] in equilibrium mixture.

proved to be difficult, and all were less effective than ethene.

The effect of diffuse background light (either daylight or artificial light) was to displace equilibrium(5-19) to the left. Observed over a period of several hours at room temperature, the ratio of $[Pt_2Cl_4(PBu_3)_2]$ to trans-$[PtCl_2(ol)(PBu_3)]$ (ol = C_2H_4, C_3H_6) was always greater in the light than in the dark (see figs. 5-4, 5-5). Unfortunately, due to the formation of the cis isomer, the equilibrium cannot be studied in isolation. Lowering the temperature to prevent isomerisation moves the equilibrium too far to the right for any accurate determination of the position. The change in equilibrium position is most likely due to photo-induced elimination from the yellow/green trans complex.

With the bromo complexes, equilibria (5-19) cannot be determined accurately enough to observe any difference between light and dark due to the very low level of trans-$[PtBr_2(C_2H_4)(PBu_3)]$ (see fig. 5-6). The situation is further complicated by the very rapid formation of the cis isomer and its known tendency to readily lose olefin and revert to the dimer. So the system cannot establish a detectable equilibrium between trans isomer and dimer in the same manner that the chloro system does.

The formation of the cis isomers from solutions containing trans-$[PtX_2(ol)(PBu_3)]$ might be expected to follow a similar pathway to that found for the carbonyl system due to the similarity of bonding in the complexes. However, accompanying any comparison of the two systems, two points must be borne in mind:-

1. Because trans-$[PtX_2(ol)(PBu_3)]$ equilibrated with $[Pt_2X_4(PBu_3)_2]$ (eqn. 5-19), free olefin must always be present in solution.

2. Cis-$[PtX_2(ol)(PBu_3)]$ could not be regarded as a "final product" in

this reaction as the cis products could revert to dimer. This is probably not a significant process for X = Cl over the time period of the reactions being studied, it would be significant when X = Br.

The formation of the cis isomer was followed for three systems, $Pt_2Cl_4(PBu_3)_2$ with ethene, or propene and $Pt_2Br_4(PBu_3)_2$ with ethene. The experimental procedure for following the isomerisations was the same for all three systems. The olefin was passed through a solution of either the chloro-or bromo-bridged dimer for 1 minute at room temperature. The solution was divided between two nmr tubes which were then capped and sealed. One tube was stored in the dark and the other kept exposed to either artificial or day-light. The reactions monitored by ^{31}P nmr spectroscopy and the relative abundance of each species was determined either by integration or by assuming that because all the signals are very sharp that the signal intensity (or height) is proportioned to the signal area. Integration showed that this latter method was as accurate as the first. (Whichever was used, it was important to remember that the intensity of the central signals only accounts for 66% of a monomeric complex and 44% of a dimeric one due to the presence of the Pt satellite signals). The results are shown in figs. 5-4, 5-5 and 5-6. It can be seen that the results for the two chloro complexes are broadly similar, with the extent of isomerisation being slightly greater for C_2H_4 than C_3H_6. (This is despite the concentration of the trans complexes being the other way round with C_3H_6 greater than C_2H_4). This reflects the greater stability of the ethene complex over the propene complex as explained above. Also the side group on the propene will cause a twisting motion in the ligand as shown in fig. 5-3, reducing the metal-π^* overlap and hence the strength of the metal-olefin bond.

The formation of the cis-bromo complex is much more rapid, reaching

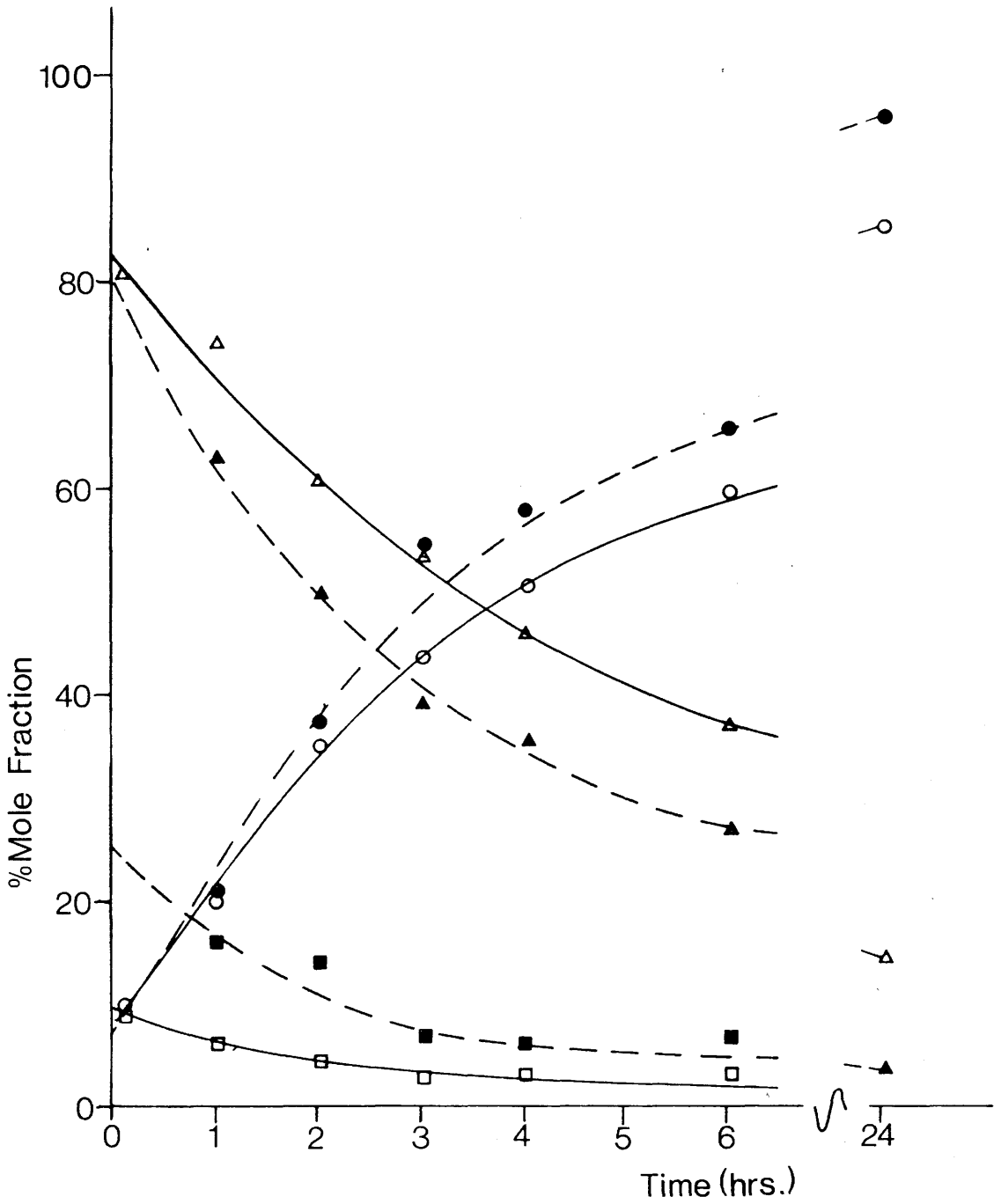


Fig 5-4 Products from the reaction $[Pt_2Cl_4PBu_3)_2]$ + C_2H_4

(Key follows Fig 5-6)

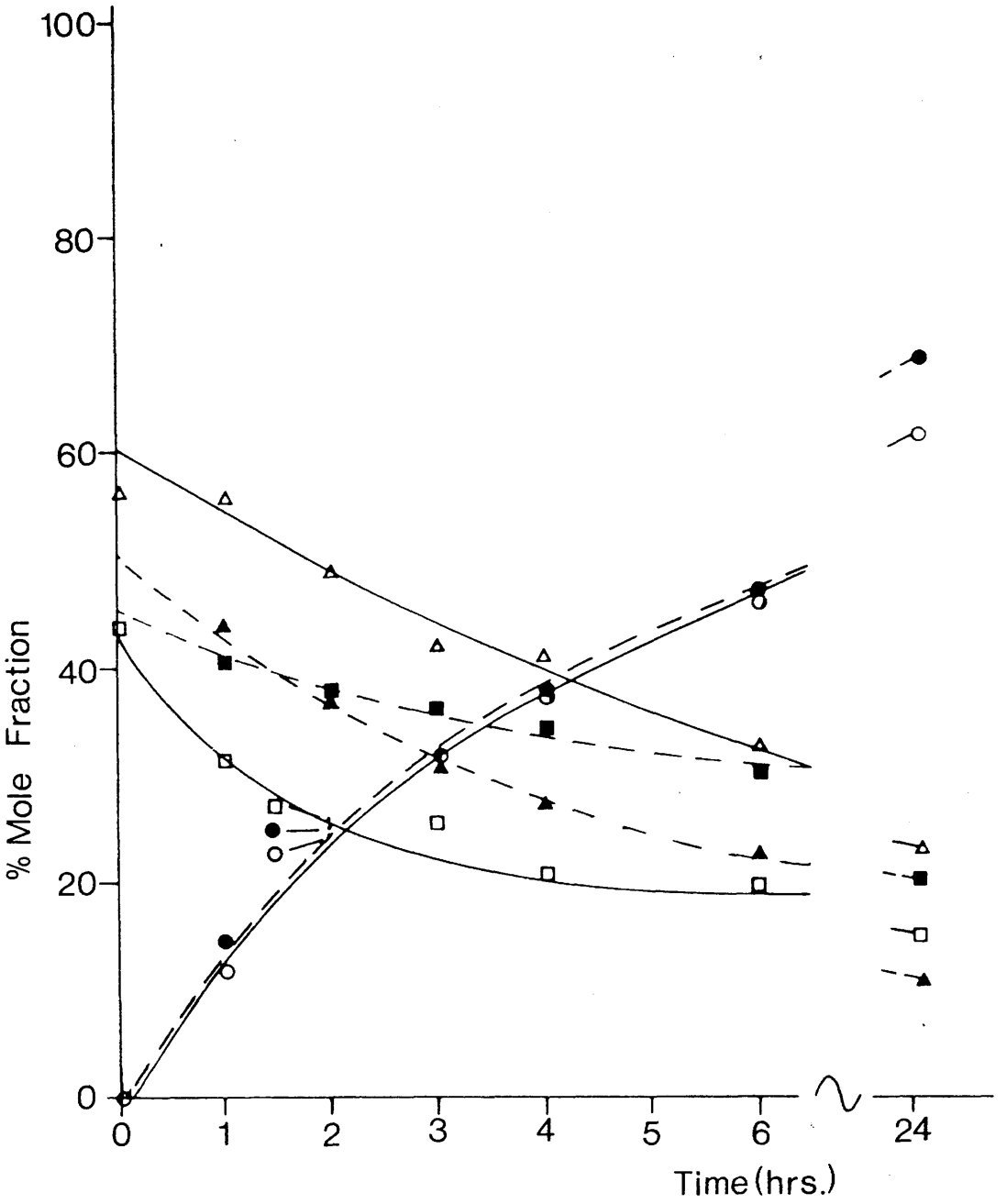


Fig. 5-5. Products of the reaction between $[Pt_2Cl_4(PBu_3)]$ and C_3H_6

(Key follows Fig. 5-6)

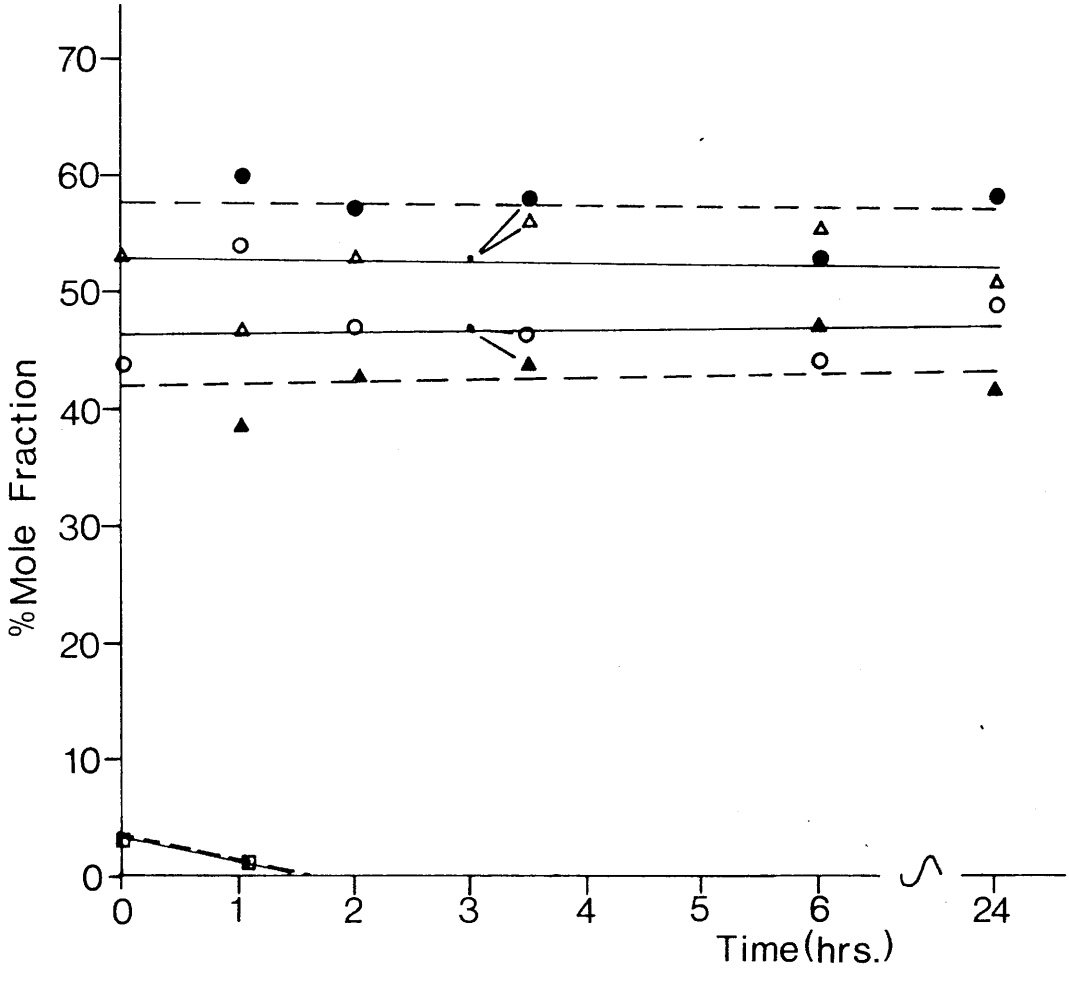


Fig. 5-6. Products from the reaction of

$[Pt_2Br_4(PBu_3)]$ and C_2H_4

(Key overleaf)

Key to Figs. 5-4, 5-5 & 5-6.

Reaction of $[Pt_2X_4L_2]$ & ol

○ & ●	refer to	cis-$[PtX_2(ol)L]$
□ & ■	" "	trans-$[PtX_2(ol)L]$
△ & ▲	" "	$[Pt_2X_4L_2]$

Solid lines represent reactions performed in daylight

Broken " " " " " dark

a maximum level within 1 hour. Because of this trans-$[PtBr_2(C_2H_4)(PBu_3)]$ could not be prepared in the absence of the cis-isomer at room temperature. It has already been reported[181] that trans bromo olefin complexes isomerise to cis at lower temperatures than the analagous chloro complexes and the rate of isomerisation of $[PtX_2(CO)(PMe_2Ph)]$ was found to be $I \gg Br > Cl$[106] consisted with the above results. With $Pt_2X_4(PMe_2Ph)_2$ the same results were found with a much more rapid formation of cis-$[PtX_2(C_2H_4)(PMe_2Ph)_2]$ with X = Br then X = Cl, although precipitation of the cis complexes prevented an accurate comparison.

Whilst figures 5-4 and 5-5 clearly show the effect of light on the dimer/trans equilibrium, at the same time they also show that the overall formation of the cis isomer is largely unaffected by alteration of this equilibrium. This could be interpreted in two ways -

1. Although the amount of trans isomer is less in the light, it can react more quickly to produce cis via a photochemical pathway, or
2. More than one reaction pathway operates to produce cis and the difference in rates due to changing concentrations for the various pathways cancel each other out by chance.

Since reactions performed totally in the dark still produce the cis isomer, a photochemical route cannot be the only one operating, and a mixture of reasons (1) and (2) is nearer the true situation.

Maintaining a large excess of olefin also had an effect on the isomersation rate. The excess olefin was provided by maintaining a constant flow of gas through the solution being studied. The effect on the production of cis-$[PtX_2(ol)(PBu_3)]$ (X = Cl, ol = C_2H_4, C_3H_6; X = Br, ol = C_2H_4) is shown in Table 5-6, where the figures in the column marked "1 min olefin" refer to solutions treated with olefin for 1 minute and

Table 5-6 Effect of excess olefin on the production of cis-$[PtX_2(ol)(PBu_3)]$

X	1min C_2H_4 [a]	1hr C_2H_4	1min C_3H_6	1hr C_3H_6
Cl	33	16	19	12
Br	65	69	0	0

(a) % of cis isomer present in solution $= \frac{[cis]}{[cis] + [trans] + [dimer]} \times 100$

left to stand for 1 hour at room temperature, whereas those marked "1 hour olefin" are for solutions treated constantly with olefin for 1 hour. It can be seen that for the chloro case excess olefin causes a retardation of the rate of formation of the cis-isomer, whereas for the bromo case the formation of cis$[PtBr_2(C_2H_4)(PBu_3)]$ was increased slightly, although after 1 hour, the bromo reaction appears to be in equilibrium (fig. 5-6) and the result is more likely to represent a shift in this equilibrium rather than the rate of formation of the cis isomer. These results contrast markedly with the analogous carbonyl isomerisations, where excess CO was found to catalyse the reaction of the chloro complexes to a great extent with the rate increasing by two orders of magnitude.

Figure 5-7 shows the possible pathways from the starting materials to cis-$[PtX_2(ol)L]$, all of which are plausible mechanisms for isomerisations in square planar compounds[23]. The most straightforward formation of the cis-isomer is by the direct cleavage of the dimer at the metal-halide bond cis to the phosphine to produce the product, represented by pathway [A]. This would compete with the faster reversible formation

$$2\text{cis-}[PtX_2(ol)L] \xleftarrow{\text{slow}} [Pt_2X_4L_2] + 2ol \overset{\text{fast}}{\rightleftharpoons} 2\ \text{trans-}[PtX_2(ol)L] \qquad (5\text{-}21)$$

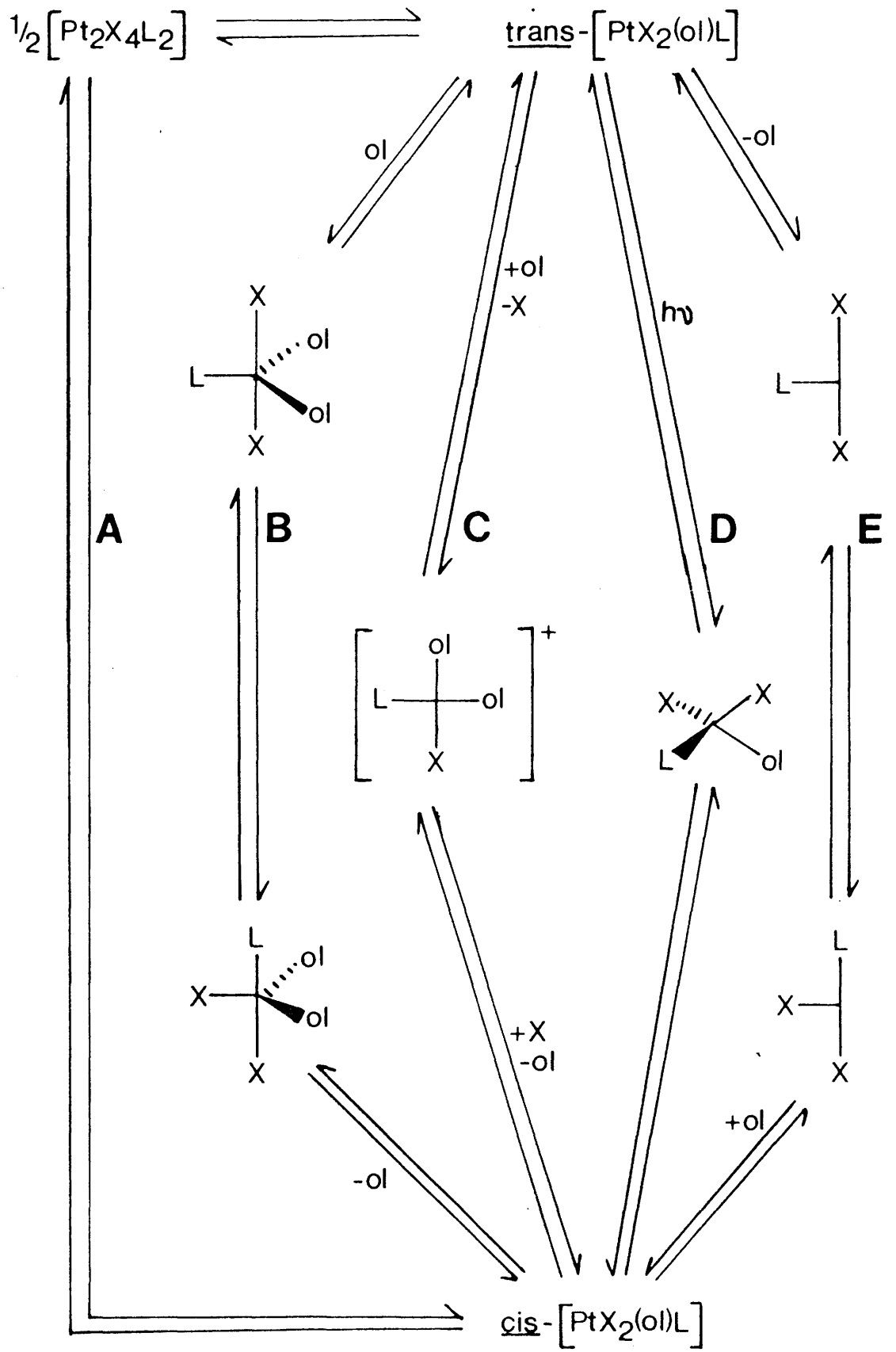
of the trans isomer (eqn. 5-21) and such a route was originally proposed for the formation of the cis-carbonyl complexes[186] although it was later shown not to be applicable in that case[106]. In the present system the pathway is consistent with three experimental observations.

1. The rate of formation of the cis complex is slightly greater for ethene than propene. The concentration of dimer is also greater for ethene than propene.

2. Bromo complexes isomerise faster than the chloro complexes.

3. Excess olefin inhibits the isomerisation of the chloro complexes.

Fig.5-7 Possible Mechanisms for the Formation of cis-$[PtX_2(ol)L]$



1., although fitting the direct route, can also be explained in terms of stability of the products. For 2. a very low value of K in equilibrium (5-19) means that the concentration of $[Pt_2Br_4(PBu_3)_2]$ and C_2H_4 are higher than for the chloro case and the rate of formation (rate $\propto [Pt_2Br_4(PBu_3)_2][C_2H_4]$) should be greater. Against this argument is the observation that cis- $PtX_2(CO)(PMe_2Ph)$ is also formed more rapidly when X = Br than X = Cl and this pathway is known not to operate in this case. 3., the inhibition in the chloro case comes from two competing factors. The removal of dimer in trans- $PtCl_2(ol)L$ via equilibrium (5-19) depends on $[olefin]^2$, whereas, because attack of the first nucleophile in a bridge cleavage reaction is usually rate determining[188], the direct formation of cis would be proportional to [olefin]. Thus the overall formation of the cis isomer would vary inversely with olefin concentration.

Pathways [B]and [C] represent catalytic isomerisation via nucleophilic attack, and is the most common isomerisation route found in square planar complexes[23]. [B] represents the pathway through a five co-ordinate intermediate, which can then undergo pseudo-rotation and ligand elimination, whereas pathway [C] shows the isomerisation proceeding via associative consecutive ligand displacement. These two pathways, however, merely represent the two extremes of one single process[189], in particular the extremes of bonding between the metal and axial ligand in a square planar transition state.

Pathway [B] is the most important isomerisation route of trans- $PtX_2(CO)L$, where CO (arising either from CO loss from the trans complex, or by deliberate addition of excess CO) acts as a nucleophile (eqn. 5-16). That such a pathway operates for the olefin complexes seems highly likely, since it was shown that both cis and trans complexes undergo rapid, stereoretentive olefin exchange (eqn. 5-18,

5-20). Furthermore, many 5 co-ordinate Pt-olefin complexes of the type $PtX_2(N\text{-}N)(ol)$ have been isolated[190]. The overall pathway represented by [B] is shown in fig. 5-8. The conventional stereospecific ligand exchange is represented by the direct pathways from A to B and C to D for trans and cis-$[PtX_2(ol)L]$ respectively. It can be seen that after olefin co-ordination to species A, then, if there is rotation about the X-Pt-X axis, giving a transition state with phosphine and two olefins in the trigonal plane, the olefin exchange pathway will be followed. However, a different rotation around the L-Pt-(ol) axis will lead to transition state E. This time the transition state has just one π-acceptor ligand in the trigonal plane and would be expected to be a less stable species than when three were present. This pathway must also be of higher energy than the ligand exchange (since the latter will go rapidly at $-60^{\circ}C$, but the former does not start until $> -20^{\circ}C$), probably due to the lower stability of the transition state. Further rotation from E can lead to the cis complexes via complex F and olefin loss to D.

If the axial halide is lost from complex E then the intermediate cis-$[PtX(ol)_2L]$ would be formed. Subsequent attack by X^- would reform E and continue the isomerisation. This would convert the process to one of consecutive ligand displacement, as represented by pathway [C] in fig. 5-7, although the overall result would be same as for [B.]

Although, by analogy to the carbonyls, an attractive mechanism in this case, the inhibition by excess olefin of the trans to cis isomerisations for the chloro complexes suggests that it cannot be the sole, or even the major mechanism in these reactions, as the inhibition implies a dissociative pathway. The slight acceleration or increase in the amount of cis for the bromo complexes is consistent with the mechanism, yet the effect of excess olefin is harder to quantify, due to

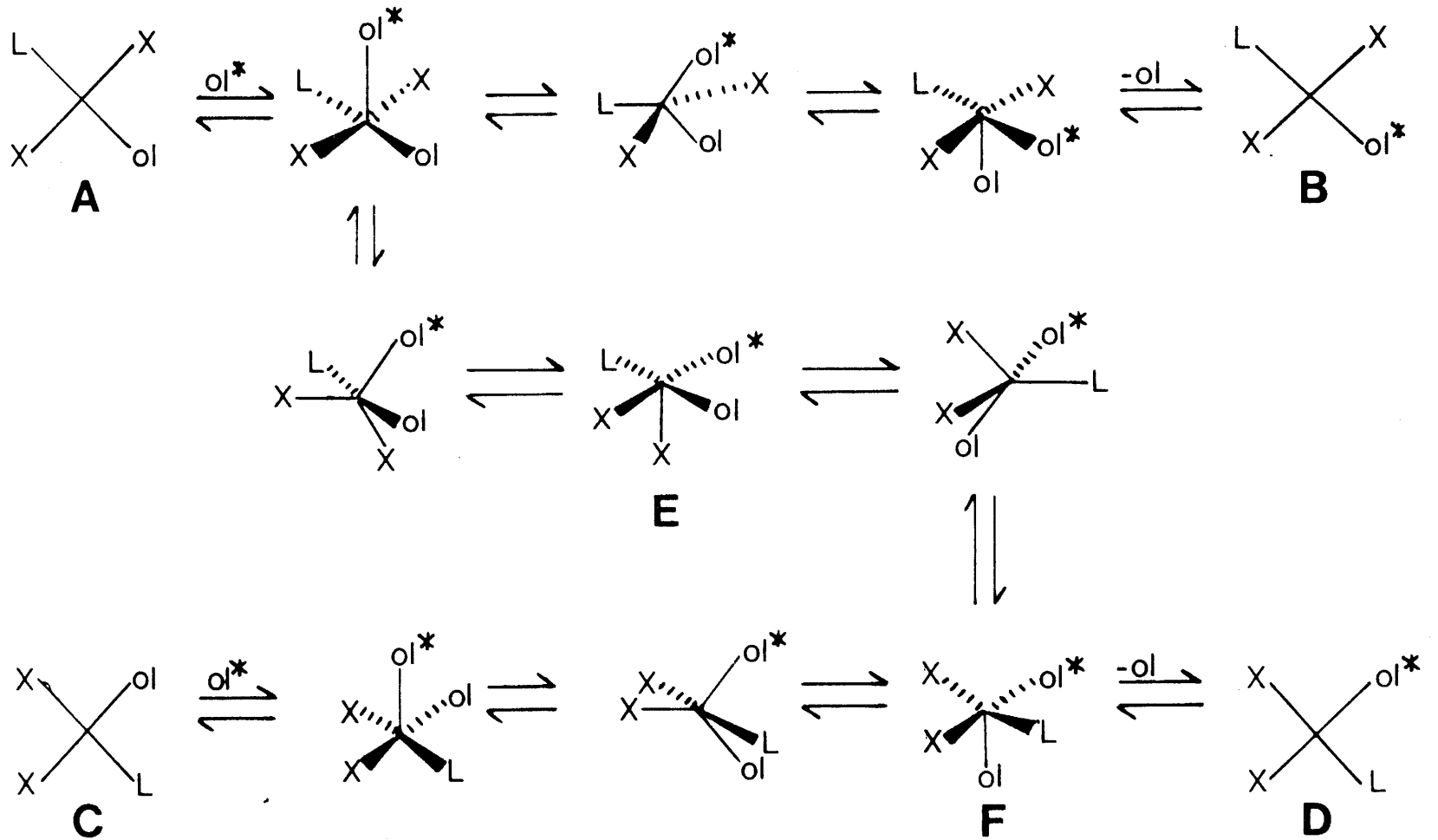


Fig. 5-8 Olefin Exchange and Isomerisation in $[PtX_2(ol)L]$

equilibrium (5-19) lying well to the left for this halide.

Non-dissociative photochemical isomerisations of square planar complexes are represented by pathway [D]. Such photochemical isomerisations have been observed for other Pt-olefin complexes such as $[PtCl_2(C_2H_4)(NR_3)]$ [191]. In the present case it is possible that as well as affecting the position of the initial equilibrium (5-19) light is having an accelerating effect on the trans → cis isomerisation step. However, even if a light catalysed pathway is operating, it cannot be the only one, as isomerisation still proceeds just as quickly (or slightly faster) in the dark.

One more pathway that must be considered is shown by pathway [E] in fig. 5-7. This involves dissociation of a ligand from a square planar complex to form a 3 co-ordinate, 14-electron, 'T'-shaped intermediate which then undergoes isomerisation before an incoming ligand rejoins the group. The importance of solvation of both the leaving group and the transition state has been demonstrated [189,192]. Although the mechanism must be regarded as controversial for Pt(II) complexes, it is known to occur in certain isomerisations of isoelectronic Au(III) species (see Chapter 2-2). Certainly olefin loss from the trans complex must occur at some point when the dimer is reformed, and a geometry change of the intermediate before dimer reformation could lead to cis- products as shown in pathway [E.] This mechanism fits the observed retardation by excess olefin on the isomerisation of the chloro complexes, but even with a vast excess of olefin the isomerisation is not stopped completely. The faster reactions of the bromo complexes are harder to explain as a very pronounced cis effect from the halide would be required to greatly increase the rate of formation of the 3 co-ordinate intermediate, or a very much faster geometry change of the 'T'-shaped intermediate. Neither

explanation seems very likely and so, like the other pathways, [E] seems plausible but cannot be the dominant route to the cis isomers.

In conclusion then, the isomerisation cannot be accounted for by one pathway alone. A photochemical pathway must be involved to allow for the effect of light on equilibrium (5-19), and retardation by excess olefin for the chloro case at least, suggests a dissociative pathway, which may be photochemical, or a direct cleavage of the dimer in the position cis to the phosphine. For the bromo case, olefin catalysed associative isomerisation seems best to describe the situation. However, given that chloro and bromo ligands have virtually the same cis and trans influence, and bromo has only a slightly greater trans effect[193], then there is no major change in the nature of the complexes between the two systems and any difference between them is likely to reflect only a change in the relative rates of the pathways operating. The best conclusion that can be drawn is that more than one non-photochemical pathway operates.

5-6.2 - The reactions of non-gaseous olefins with $[Pt_2X_4(PR_3)_2]$

The main problem with using ethene and propene was that it was impossible to tell how much of either olefin was in solution at any time, as this would depend on temperature and the ratio of co-ordinated to free alkene. It was thought that by using liquid alkenes the exact stoichiometry of the reactions could be controlled. (Solid alkenes could also have been used for this purpose, although in practice none were).

The reaction between $[Pt_2X_4(PBu_3)_2]$ and hept-1-ene ($C_5H_{11}CH=CH_2$) was only partially successful. To two samples of $[Pt_2Cl_4(PBu_3)_2]$ was added either 1.8 or 2.2 equivalents of heptene. Both samples rapidly formed an equilibrium between dimer and a species with ^{31}P nmr parameters

δ_p 5.2ppm J_{PtP} 3364 Hz (measured at -60°C) which was assigned to trans-$[PtCl_2(C_7H_{14})(PBu_3)]$ by analogy to the ethene and propene complexes (see Table 5-6). Excess olefin had the expected effect of moving the equilibrium to the right (as shown in eqn. 5-19), so that with 10% deficiency of olefin, there was 28% of the trans complex at -60°C, but with 10% excess, 34%. (These values contrast with those for the gaseous alkenes, where at -60°C there was no dimer present). Warming to room temperature caused complete olefin loss from the dimer, indicating that the trans olefin complex from heptene is considerably less stable than that containing C_2H_4 or C_3H_6. With larger excesses of heptene (10-fold excess) equilibrium (5-19) was detectable even at room temperature ($K \simeq 1$) although signals for both dimer and the trans complex were broad, indicating that olefin loss from the trans complex and re-attack at the dimer was rapid on the nmr timescale. Sharp signals for a third complex were present after only 5 minutes in this case, at δ_p 3.6ppm, J_{PtP} 3089 Hz. This complex steadily grew in until after 5 days it accounted for 67% of the phosphorus containing products. This is assigned to cis-$[PtCl_2(C_7H_{14})(PBu_3)]$, again by anology to the gaseous alkene complexes. The fact that it was formed quite rapidly initially points to excess olefin accelerating the rate. (No such complex was apparent even after 3 hours with around 2 equivalents of heptene.) This is due either to increasing the amount of trans complex and so causing an increase in rate, or else by promoting direct formation from the dimer. Whichever the pathway, the result contrasts sharply with the behaviour of $PtCl_2(CH_2{=}CHR)(PBu_3)$ (R = H,Me).

With $[Pt_2Br_4(PBu_3)_2]$, there was no cleavage of the halide bridge, even using heptene in large excess and at low temperature, again reflecting the increased strength of the halide bridge and the lower stability of the heptene complexes. Attempts to prepare cis-$[PtBr_2$-

$(C_7H_{14})(PBu_3)]$ by ethene displacement from cis-$[PtBr_2(C_2H_4)(PBu_3)]$ led to a small amount of two new species with ^{31}P nmr parameters $\delta 3.6$ J_{PtP} 3020 Hz and $\delta 3.4$ J_{PtP} 3020 Hz, which were possibly due to some of the cis-heptene product with two signals produced due to the two different isomers (a) and (b) as shown in fig. 5-9. Such enatiomeric formation

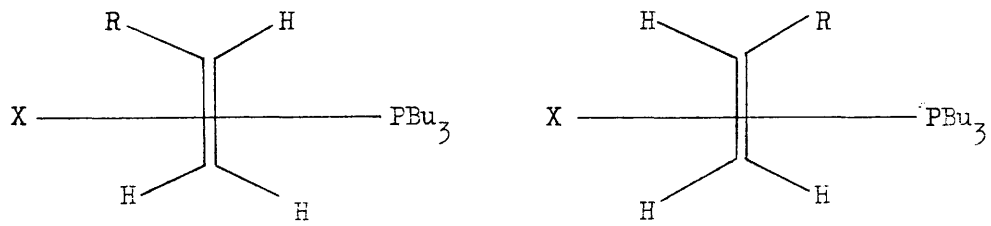


Fig. 5-9 Possible isomers of cis- $PtBr_2(C_7H_{14})(PBu_3)$

has been reported previously, and by replacing the phosphine with an optically active amine, the two isomers of cis-$[PtCl_2(ol)(NHEtPh-\alpha)]$ have been separated by fractional crystallisation[194] for propene, and t-butylethene. Similar optical isomers were also observed for the trans complexes, and it was found that treatment of the complexes with excess olefin led to racemisation due to olefin exchange, with trans racemising faster than cis due to faster exchange. That no such mixture of isomers was observed for trans-$[PtCl_2(C_7H_{14})(PBu_3)]$ could be due to the fact that it was only observed under conditions with a large excess of heptene present.

Methylacrylate (CH_2=$CHCO_2Me$) and acrylonitrile (CH_2=CHCN) were even less successful than heptene in forming Pt-olefin complexes. Methylacrylatehad no effect on $[Pt_2Cl_4(PBu_3)_2]$ when added in stoichiometric amount. Furthermore, in a separate experiment, when methylacrylate was added to a solution of cis-$[PtCl_2(C_2H_4)(PBu_3)]$ again no reaction occurred. Acrylonitrile, on the other hand, did react with $[Pt_2Cl_4(PBu_3)_2]$ to produce a new species with parameters δ_P 6.2ppm P_{PtP} 3789 (at room temperature). This species grew in steadily but

slowly until after 6 days the dimer and new species were present in equimolar amounts. The nmr signals were broad, but on cooling the sample to -60°C they sharpened considerably and the relative amounts of the two species changed, so that at low temperature the dimer accounted for only 10% of the mixture. The coupling constant of the new species is not consistent with an η^2-olefin complex, and it seems likely that the acrylonitrile is acting like an amine (eqn. 5-22) with the formation of a Pt-N bond (see chapter 4). The equilibrium (5-22)

$$\left[Pt_2Cl_4(PBu_3)_2\right] + 2CH_3CHCN \rightleftharpoons 2\ \underline{trans}\text{-}\left[PtCl_2(NCCHCH_2)(PBu_3)\right] \quad (5\text{-}22)$$

must take a long time to establish, and there is no guarantee that even after 6 days it has been reached.

5-6.3 The isomerisation of $PtX_2(dmso)(PBu_3)$

In order to try and gain more information about the platinum olefin system, the reactions between $Pt_2X_4(PBu_3)$ and dimethylsulphoxide (dmso; $(CH_3)_2SO$), were also studied. This ligand, although possessing an S = O double bond does not form η^2-complexes with metals. Rather it forms ligand-metal σ-bonds either through O (if the metal is a hard acid) or S (for softer metals). For Pt(II), S-bonding is more common, e.g. $[PtCl_3(dmso)][PF_6]$[195], $[PtCl_2(dmso)_2]$[196] and $[PtCl_2(dmso)(NC_6H_4OMe\text{-}\underline{o})]$[197], although O-bonding is known, especially if steric crowding is present, and with higher homologues of the series R_2SO e.g. $[PtCl(OSMe_2)(dppe)][PF_6]$[198] and $[PtCl_2\{OS(CH_2Ph)_2\}(PCy_3)]$[199], although the latter complex will isomerise to the S-bonded form very slowly (80% after 9 months). The properties of sulphoxides S-bonded to Pt(II) have been compared to olefins[200]. From kinetic studies on $PtCl_n(H_2O)_{3-n}(dmso)$[193] it was found that both are of high and nearly equal *trans* influence, and high *trans* effect with ethene having a greater *trans* effect than dmso. Their reactivity is similar, so in the complexes $PtCl_3L^-$ (L = C_2H_4 or dmso), Cl *trans* to L is found to exchange very rapidly in both cases[193]. Also, with K = equilibrium constants for reaction (5-22) are found to be very similar/

1.5×10^8 (L = dmso) or 4.5×10^8 ($L = C_2H_4$).

$$[Pt(NH_3)_3L] + H_2O \underset{}{\overset{K}{\rightleftharpoons}} \underline{trans}\text{-}[Pt(NH_3)_2(H_2O)L] + NH_3 \qquad (5\text{-}22)$$

The reaction between $[Pt_2Cl_4(PBu_3)_2]$ and less than two equivalents of dmso have been previously described[201] and the initial rapid appearance of $\underline{trans}$-$[PtCl_2(dmso)(PBu_3)]$ which subsequently isomerised (93% over 24 hours) to the $\underline{cis}$ isomer reported. Likewise dmso reacted with $[Pt_2Cl_4(PCy_3)_2]$ to produce $\underline{trans}$-$[PtCl_2(dmso)(PCy_3)]$ which very slowly isomerised to the $\underline{cis}$ form (85% after 8 months)[199].

On addition of controlled amounts of dry dmso to $[Pt_2X_4(PBu_3)_2]$ (X = Cl,Br), $\underline{trans}$-$[PtX_2(dmso)(PBu_3)]$ was formed immediately and unless a deficiency of dmso was used, no dimer remained (at room temperature). As with the olefin studies, $CDCl_3$ solutions of the $\underline{trans}$ isomer were prepared, using either a deficiency or excess of dmso, split into separate nmr tubes and stored either in ambient light or in the dark at room temperature. The subsequent isomerisations were followed by ^{31}P nmr spectroscopy over 24 hours.

With X = Cl, the ^{31}P nmr parameters of the two isomers (see Table 5-7) agree with literature values[201]. The amount of the $\underline{cis}$ isomer produced against varying reaction conditions is shown in Table 5-8. The table shows that, like the olefin reactions, increasing the amount of dmso clearly has an inhibiting effect on the isomerisation of the $\underline{trans}$ isomer. Also diffuse daylight has a slight accelerating action on the isomerisation. The results therefore resemble those obtained for the isomerisation of $\underline{trans}$-$[PtCl_2(ol)(PBu_3)]$. It should be noted that excess dmso lowers the rate of isomerisation equally in both the light and the dark. Therefore the photochemical route cannot be purely dissociative, as the inhibition by excess dmso would be removed with the removal of the system from the light. Direct cleavage is also less likely in this case, the $\underline{cis}$-dmso complex was produced as fast as $\underline{cis}$-

Table 5-7 - ^{31}P nmr parameters of $[PtX_2(dmso)(PBu_3)]$

X	cis isomer		trans isomer	
	δ_P	J_{PtP}	δ_P	J_{PtP}
Cl	9.8	3411[a]	2.9	3121[b]
Br	10.0	3346	-0.5	3012

a) Literature values δ 9.9 J 3412

b) Literature values δ 3.0 J 3121

Table 5-8 Amount of <u>cis</u> isomer produced in <u>trans</u> → <u>cis</u> isomerisation of $[PtCl_2(dmso)(PBu_3)]$ (a)

$[dmso]$ (b)	Time — 3 hrs		6 hrs		24 hrs	
	condition — light	dark	light	dark	light	dark
0.9	67	63	83	78	95	95
1.1	60	57	73	71	86	83
2.0	56	53	69	62	-	-

(a) Values represented as $\frac{[cis]}{[cis]+[trans]}$ X 100

(b) Shown as $\frac{[dmso]}{\frac{1}{2}[Pt_2Cl_4(PBu_3)]}$

$[PtCl_2(ol)(PBu_3)]$ yet there was very little dimer present, the equilibrium analogous to (5-19) lying extremely far to the right in this case. A dissociative pathway therefore seems to describe this isomerisation best.

In the reaction with $[Pt_2Br_4(PBu_3)_2]$ again many similarities with the olefin system were found. On addition of varying amounts (from 1.8 to 4 equivalents) of dmso to $[Pt_2Br_4(PBu_3)_2]$ two new signals were produced in the ^{31}P nmr spectra at δ_P-0.5ppm J_{PtP}3012 Hz and δ_P 10.0ppm J_{PtP} 3346 Hz assigned to trans and cis-$[PtBr_2(dmso)(PBu_3)]$respectively, by analogy of their Pt-P coupling constants and chemical reactivity to $[PtCl_2(dmso)(PBu_3)]$ (see Table 4-7). Furthermore, the cis bromo complex was isolated and fully characterised. As before the cis-isomer was produced much more rapidly for the bromo complexes than the chloro ones with 90% cis isomer present after 3 hours for the former compared with 60% for the latter (see Table 5-9). The amount of cis isomer did not change after a further 21 hours, indicating that an equilibrium situation had been reached. It seems likely that there is dmso loss from the complex to give dimer with rapid re-attack to give more trans isomer (eqn. 5-23), although a cis⟶trans isomerisation cannot be ruled out. The effect of excess dmso is to slightly increase the amount of cis isomer in this equilibrium mixture.

$$\text{cis-}[PtBr_2(dmso)(PBu_3)] \rightleftharpoons [Pt_2Br_4(PBu_3)_2] \overset{dmso}{\rightleftharpoons} \text{trans-}[PtBr_2(dmso)(PBu_3)] \qquad (5\text{-}23)$$

This could be due either to excess dmso inhibiting ligand loss from the cis complex or else to dmso catalysing the trans⟶cis isomerisation step in eqn. (5-23). Light had little or any effect on the system, presumably because equilibrium is reached so fast that any difference in rate of achieving it will not be noticed.

The dmso system, then, resembles the olefin system in relative reaction rates of the chloro and bromo complexes, and the same unusual behaviour of excess ligand on the rate of isomerisation in the chloro complexes. So it would appear that again more than one pathway is

Table 5-9 Amount of cis isomer produced in the trans→cis isomerisation of $[PtBr_2(dmso)(PBu_3)]$[(a)]

[dmso]	Time / condition	3 hrs light	3 hrs dark	6 hrs light	6 hrs dark	24 hrs light	24 hrs dark
0.9		89	88	90	88	89	91
1.1		90	91	90	90	92	90
2.0		93	93	92	93	-	-

(a) as % cis isomer

operating with a dissociative pathway dominating for the chloro complexes, whilst an associative pathway is important for the bromo complexes. It should be noted that in a careful study of the trans → cis isomerisation of $[PtCl_2(dmso)_2]$ [202] it was found that trans-$[PtCl_2(dmso)_2]$ underwent ligand loss to give $[Pt_2Cl_4(dmso)_2]$ and free dmso that this dmso catalysed the isomerisation along an associative route, a situation which resembles both the bromo case above and isomerisation of trans-$[PtCl_2(CO)(PMe_2Ph)]$ [106].

5-7 Experimental

The complexes $[Pt_2Cl_4(PMe_2Ph)_2]$ [163,164] and $[Pt_2Cl_4(PBu_3)_2]$ [165,166] were prepared from K_2PtCl_4 and free phosphine. Cis-$[PtCl_2(C_2H_4)(PBu_3)]$ [186], cis-$[PtCl_2(C_2H_4)(PMePh)]$ [185] and cis-$[PtCl_2(dmso)(PBu_3)]$ [201] were prepared by literature methods.

Di-μ-bromodibromobis(tributylphosphines)diplatinum:- Excess KBr (5g) was added to a solution of $[Pt_2Cl_4(PBu_3)_2]$ (2g) in acetone (70ml). The mixture was refluxed for 2 hours, then filtered whilst hot to remove excess KBr. Solvent was removed under reduced pressure and the crude product extracted into $CHCl_3$ to remove the remaining potassium salts. Evaporation of $CHCl_3$ and recrystallisation from methanol yielded pure $[Pt_2Br_4(PBu_3)_2]$ as orange crystals. (1.63g; 63%) M.Pt. 154-155°C. Found; C,25.8; H, 4.8; P, 5.4% required for $C_{24}H_{54}Br_4P_2Pt_2$; C, 25.9; H, 4.9; P, 5.6%. ^{31}P nmr data given in Table 6-1.

Di-μ-iodoiodobis(tributylphosphine)diplatinum:- Although its ^{31}P nmr characteristics had been reported[184] no preparative details were given. It was prepared by an analogous route to above using LiI instead of KBr. All LiI dissolved in hot acetone, but on concentrating and cooling $[Pt_2I_4(PBu_3)_2]$ re-crystallised as red crystals (yield 69%) M.Pt. 156-157°C. Found: C, 21.94; H 4.11; P, 4.93%. Required for $C_{24}H_{54}I_4P_2Pt_2$; C, 22.13; H, 4.18; P. 4.76%. ^{31}P nmr data given in Table 6-1.

Cis-dibromo(dimethylphenylphosphine)(ethene)platinum:- $[Pt_2Br_4(PMe_2Ph)_2]$ (200mg) was dissolved in $CHCl_3$ (3ml). Ethene was bubbled through the solution very slowly at room temperature for 2 hours, during which time colourless crystals of cis-$[PtBr_2(C_2H_4)(PMe_2Ph)]$ grew in solution and were then isolated by filtration yielding pure product (137 mg; 65%) (see Tables 6-2 and 6-6 for physical and ^{31}P nmr parameters) M.Pt. >120(dec).

Cis-dichloro(dimethylphenylphosphine)(propene)platinum:- Propene was passed through a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ (215mg) in $CHCl_3$ (10ml) for 5 minutes at room temperature. The flask was stoppered and stored for 24 hours at 5°C during which time crystals formed. The process was repeated with propene being used to halve the amount of chloroform present. The crystals were filtered, affording pure cis-$[PtCl_2(C_3H_6)(PMe_2Ph)]$ (226mg, 95%). M.Pt. >160°C (dec). Physical and ^{31}P nmr data are given in Tables 6-2 and 6-6. I.R. ν(Pt-Cl) 278, 325cm^{-1}, ν(C=C) 1505cm^{-1}.

Cis-dibromo(tri-n-butylphosphine)(ethene)platinum:- This was prepared similarly by passing ethene through a solution of $[Pt_2Br_4(PBu_3)_2]$ in $CHCl_3$/light petroleum (60-80°C) and storing for 24 hours. White crystals of pure cis-$[PtBr_2(C_2H_4)(PBu_3)]$ were isolated. M.Pt. >95°C (dec). ^1H $\delta_{C_2H_4}$ 4.39 J_{HPt} 61 Hz. I.R. ν(C=C) 1515cm^{-1}.

Cis-dibromo(dimethylsulphoxide)(tributylphosphine)platinum:- The solutions from 4 nmr scale isomerisations of $[PtBr_2(dmso)(PBu_3)]$ (each starting from 23.8mg of $[Pt_2Br_4(PBu_3)_2]$ plus varying amounts of dmso in ½ml $CHCl_3$) were combined and solvent slowly evaporated until yellow crystals of cis-$[PtBr_2(dmso)(PBu_3)]$ formed, which were then isolated. M.Pt. 117-118°C. Found; C, 26.67; H, 5.30; Br 23.01%. Required for $C_{14}H_{33}Br_2OPPtS$; C, 26.47; H, 5.24; Br, 25.15%. ^1H δMe 3.65 $^3J_{HPt}$ 23 Hz.

Attempted prep. of trans- $PtCl_2(C_2H_4)(PMe_2Ph)$:- Ethene was bubbled through a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ in benzene for 10 minutes, during which time the colour of the solution changed from orange to green. The solution was rapidly frozen and solvent removed by sublimation, leaving a yellow powder, which was stored in the dark at -78°C. Microanalysis and nmr spectroscopy showed that the solid was starting dimer. Treatment of this solid with more C_2H_4 still failed to produce

any trans-$[PtCl_2(C_2H_4)(PMe_2Ph)]$.

Isomerisation of Pt-olefin complexes:- These were all performed on a small scale, typically 20-30mg of $[Pt_2X_4L_2]$ and followed by ^{31}P nmr spectroscopy. A typical example is given.

Isomerisation of $PtCl_2(C_2H_4)(PBu_3)$:- Through a solution of $[Pt_2Cl_4(PBu_3)_2]$ (20mg) in $CDCl_3$ ($\frac{1}{2}$ml) was passed C_2H_4 gas for 1 minute at room temperature. The sample was transferred quantitatively into an nmr tube and sealed. The isomerisation was followed by regular monitoring of the sample by ^{31}P nmr spectroscopy.

Olefin exchange studies of trans $PtX_2(ol)(PBu_3)$:- $[Pt_2X_4(PBu_3)_2]$ (20mg) was dissolved in $CDCl_3$ (0.5ml) and C_2H_4 passed through the solution for 2 minutes at room temperature. The sample was cooled to -60°C and ^{31}P nmr spectroscopy detected only trans-$[PtX_2(C_2H_4)(PBu_3)]$. The solution was maintained at -60°C in an acetone/dry ice bath and C_3H_6 was passed through the solution for 2 minutes. (Caution and speed had to be exercised in all manipulations as C_3H_6 liquid at this temperature, and even on slight warming during transfer into the nmr probe, violent evaporation was liable to take place). ^{31}P nmr spectroscopy confirmed that all ethene had exchanged for propene. By repeating the process with C_2H_4 the exchange could be reversed.

Dmso and heptene isomerisations reactions:- These were performed as for the olefin isomerisations, except that dry dmso or heptene were introduced to the solution in stoichiometric amounts by addition of the ligand with micro-syringes.

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